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Enviro Control, Inc, Rockville, Md

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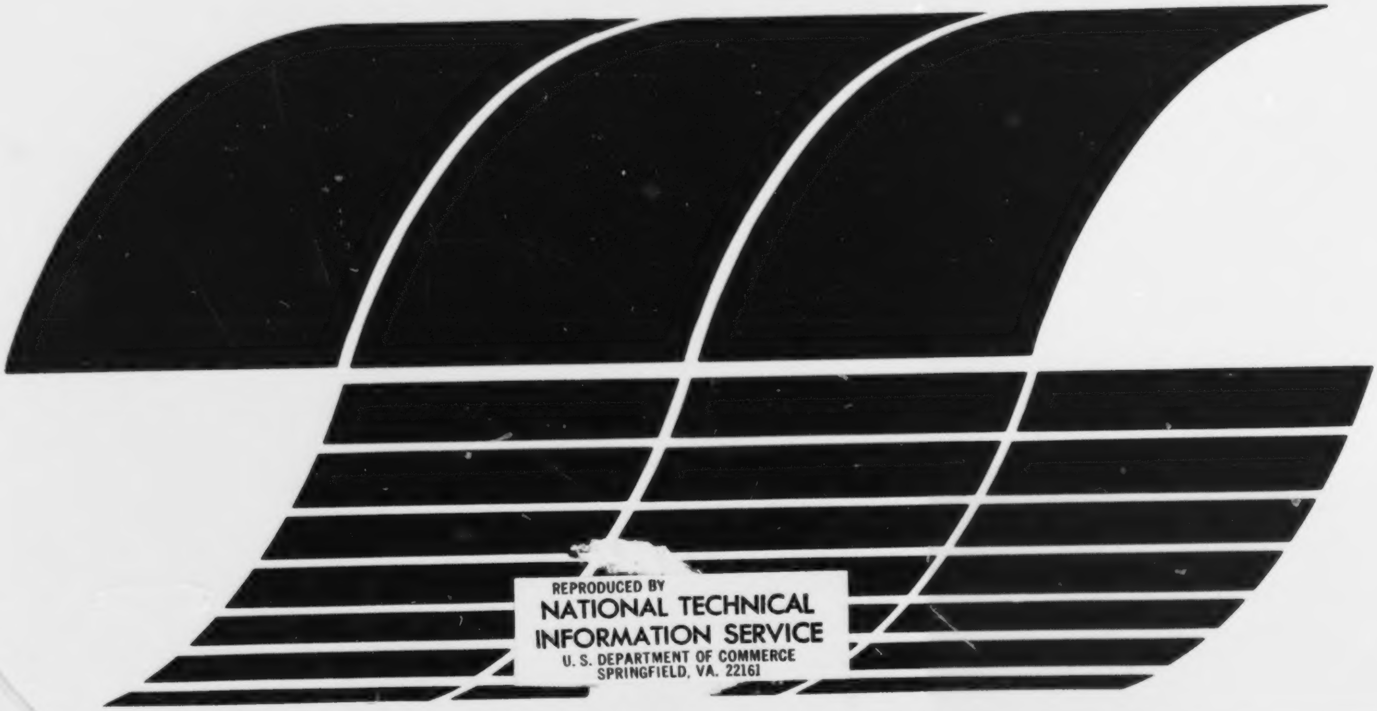

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16. ABSTRACT

These guidelines are deemed appropriate for the pilot plant stage of development of advanced coal gasification technology. They are based on pilot plant experience thus far in the United States; and on known hazards and control procedures in analogous industries. Those responsible for health protection require information that can apply to their specific problems and operations. The document is designed to help the user by presenting evidence and rationale that can be evaluated and modified or adjusted for application to individual circumstances.

A representative process is described in detail and significant differences in other processes are noted. Toxicants and potentially hazardous operations are identified. Health effects associated with the toxicants are reviewed. Guidelines for worker protection are prescribed, including engineering controls, work practices, workplace monitoring, medical surveillance, and personal protection. Monitoring procedures are recommended to meet the perceived needs for environmental sampling and medical surveillance. Safety hazards are discussed and safety measures are presented. Recommendations are made for research and development to meet identified gaps in knowledge and technology for worker health and safety protection.

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January 1978

DISCLAIMER

The Division of Criteria Documentation and Standards Development, National Institute for Occupational Safety and Health, had primary responsibility for development of the recommended health and safety guidelines for coal gasification pilot plants. The division review staff for this document consisted of Richard A. Rhoden, Ph.D. (chairman), Frank L. Mitchell, D.O., and Paul E. Caplan.

Enviro Control, Inc., prepared the document under contract No. 210-76-0171 for consideration by NIOSH staff. Murray L. Cohen had NIOSH program responsibility and served as Project Officer.

The views expressed and conclusions reached in this document are the result of careful review of the available evidence, and consideration of comments from external reviewers. These views and conclusions, however, are not necessarily those of the external reviewers or of the contractor.

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PREFACE

The Occupational Safety and Health Act of 1970 emphasizes the need for standards to protect the health and safety of workers exposed to an ever-increasing number of potential hazards at their workplace. The National Institute for Occupational Safety and Health has projected a formal system of research, with priorities determined on the basis of specified indices, to provide relevant data from which valid criteria for effective standards can be derived.

This document has been developed as part of the Interagency Energy and Environment Research and Development Program. It's purpose is to identify potential hazards to workers in coal gasification pilot plants, and to develop hazard control strategies. The guidelines emphasize worker protection measures such as safe work practices, personal protective equipment and clothing, industrial and personal hygiene, workplace and medical monitoring, labeling and posting, hazard information and awareness, and recordkeeping.

Although this document is specific for pilot scale coal gasification plants, many of the potential hazards and research and development needs are similar to those in bench or demonstration scale coal gasification or coal liquefaction facilities. The recommended health and safety guidelines are in many ways applicable to these facilities as well. This document should also be a valuable reference for researchers and administrators responsible for the development and operation of these related coal conversion implementation of these guidelines in experimental coal conversion facilities will not only help protect the health and safety of today's workers, but will also make occupational health and safety research an integral part of the development of coal conversion technology. In this way, hazards can be identified and effective control technology can be developed prior to the design and construction of commercial coal gasification plants.

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INTRODUCTION

NEED FOR HEALTH AND SAFETY MEASURES

The United States Energy Research and Development Administration estimates that by the year 2000 coal gasification products will be supplying 8.6 X 10^{15} Btus/year towards our national energy demand (Energy Research and Development Administration 1976), at which time this industry may employ 140,000 workers. To develop coal gasification technology, the Federal Government and private industry are investigating at least 21 different approaches at the theoretical, bench, or pilot plant stages. Currently there are 16 pilot plants either in operation or expected to begin operation within the next 3 years, each employing between 80 and 200 workers.

The pilot plant worker may be exposed to chemical and physical health and safety hazards. The potential toxic hazards are the focus of this document because they may cause serious health effects. These hazards are generally less well understood than the other hazards, and protective measures against them are less well established. The toxic hazard potentials are assessed on the basis of the known presence of a variety of toxicants in process streams and wastes, the probability of emissions through leaks and equipment failure, and the necessity for opening, and perhaps entering, equipment.

The presence of potential toxic hazards, including that of exposure to chemical carcinogens, is established. Therefore, measures that protect the health and safety of coal gasification workers are needed.

PRIORITY GIVEN TO PILOT PLANTS

The focus of this document is on pilot plants for the following reasons: Several of the coal gasification pilot plants are now in operation, and they may be without adequate control measures to protect worker health and safety. A special approach to develop these measures is required because pilot plants are, in addition to size differences, significantly different from demonstration and commercial scale plants in operational characteristics. No commercial plant, based on present pilot plant technology, will be in operation in the United States before 1985 at the earliest. The pilot plants are the only observable domestic models of working conditions. Their study will provide a useful and appropriate basis for future development of recommended standards for occupational safety and health protection in commercial coal gasification plants.

CHARACTERISTICS OF PILOT PLANTS

The pilot plant is a hybrid of specially designed and makeshift equipment. Although it is much larger than a laboratory unit, by a factor of perhaps 100, little of its equipment would be useful in a commercial-size plant. Apart from the gasifier, few of the components have been designed for the highly specialized operating conditions of coal gasification. Even with the best of engineering know-how, exploration of new processes is attended by unforeseen problems and failures. This is one of the major reasons for the pilot plant stage of process development.

The pilot plant is designed primarily to obtain process data in order to define the engineering specifications required to build larger plants, determine the best materials of construction, and develop work practices and equipment for optimum operation. Process testing often occurs under non-optimum conditions, which may cause run failure. In this event, the entire plant is generally shut down, as there is insufficient surge volume to permit one section to run independently of the others. Thus, frequent shutdown, cleanup, repair, modification, maintenance, and start-up constitute major portions of the pilot plant cycle. Due to the continual replacement of equipment, a coal gasification pilot plant will have less than 35% onstream operating time.

Pilot plants may therefore be expected to have more leaks, be subject to more emergencies, and undergo much more dismantling of equipment for maintenance, repair, or modification than commercial scale plants.

CHARACTERISTICS OF EXPOSURE AND PERTINENT HEALTH DATA

The pilot plant worker may be exposed to toxicants by inhalation of gases or airborne particles, skin deposition of airborne material, contact with contaminated surfaces, and accidental ingestion. In maintenance operations, liquid and solid residues may be encountered that would not ordinarily constitute normal operational hazards.

The range of toxicants and possible health effects is extremely wide, from simple chemicals like carbon monoxide to complex mixtures of organic carcinogens. This complexity is further complicated by the special problems associated with carcinogens: long latent period, doubt about "safe" levels, and unpredictable multiagent interactions.

These conditions cannot be met by protective measures, monitoring procedures, and medical tests that are simply the sum total of controls for each individual toxicant. The complexity of the potential hazards calls for innovative control strategies.

Few data are available concerning the workplace environment and other occupational health factors in coal gasification plants. The somewhat better documented health hazards of coke ovens, coal liquefaction, and similar plants are relevant, but not fully acceptable as models for coal gasification.

APPROACH TO DOCUMENT DEVELOPMENT

Because of the foregoing considerations, this document has been oriented towards processes rather than towards specific toxic hazards. The sequence and structure of the document are as follows:

- A representative process is described in detail and significant differences in other processes are noted.
- Toxicants and potentially hazardous operations are identified.
- Health effects associated with the toxicants are reviewed, including diseases observed in association with coal processing.
- On the basis of identified potential hazards, guidelines for worker protection are prescribed: engineering controls, work practices, workplace monitoring, medical surveillance, personal protection.
- Monitoring procedures are recommended to meet the perceived needs for environmental sampling and medical surveillance.
- Safety hazards are discussed, and safety measures are presented.
- Recommendations are made for research and development to meet identified gaps in knowledge and technology for worker health and safety protection.

THE DOCUMENT

These guidelines are deemed appropriate for the pilot plant stage of development of advanced coal gasification technology. They are based on pilot plant experience thus far, and on known hazards and control procedures in analogous industries. It is recognized that no two coal gasification pilot plants are alike in process technology or hazards. Additionally, workplace conditions are variable at any one plant.

Those responsible for health protection require information that they can apply to their specific problems and operations. The document is therefore designed to help the user by presenting evidence and rationale that can be evaluated and modified or adjusted for application to individual circumstances.

COAL GASIFICATION: PROCESS DISCUSSION

INTRODUCTION

Coal

Coal, as shown schematically in Figure 1 below, is derived from decayed plant material laid down in the vast swamps which covered large areas of the northern hemisphere during the lower carboniferous to tertiary periods. This decayed material (peat) was subjected to a variety of microbiological, geophysical, and geochemical conditions, which varied not only from one section (or swamp) to another but also within local regions. Consequently, any quantitative statement concerning the composition, structure, and products of coal is subject to variation, even for coal mined from the same general section of a specific coal seam.

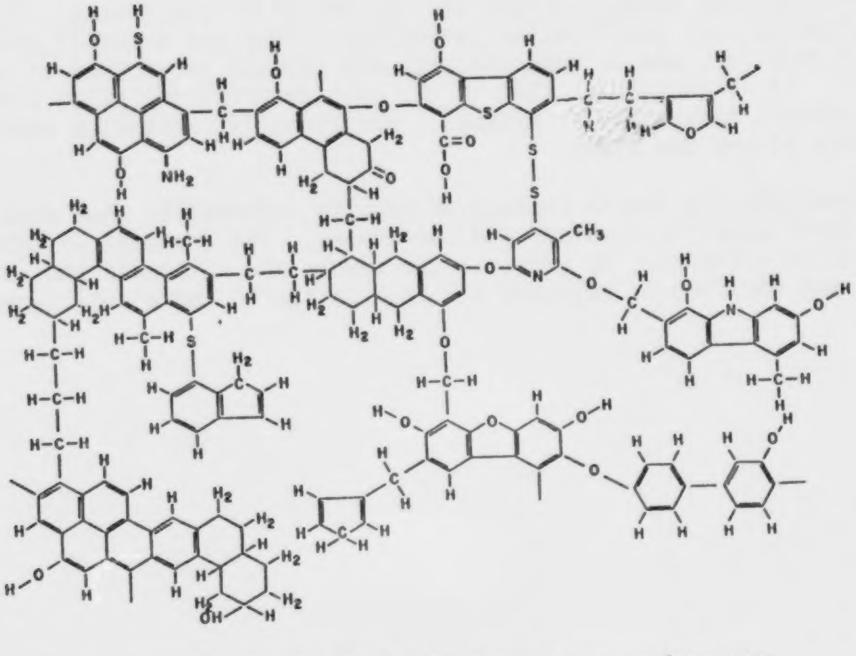

Figure 1. Representation of high-volatile bituminous coal structure (Wiser 1973).

Coal is "ranked" systematically according to volatile matter and heat content (Btu/lb). Coal rank depends on the extent of "coalifaction" and varies sequentially from the low-rank lignite through sub-bituminous and bituminous to high-rank anthracite. In general, carbon content increases and volatile matter decreases with increase in rank, while oxygen content correlates with decreasing rank.

Coal is composed of organic and inorganic matter (up to 50%). The organic elements include carbon, hydrogen, oxygen, nitrogen, and sulfur, all of which are combustible except oxygen. The inorganic mineral matter present is associated partly with the coal (organometallic) but primarily with the ash, which ranges from 3-20 wt % in commercial coals and averages about 10 wt %. Ash content reflects the degree of care in both mining and cleaning as well as the intrinsic grade or quality of the coal itself. The variability of coal composition is illustrated by the values for 101 bituminous coals shown in Table 1. In short, coal is probably the most highly variable fuel used by man. The products of any given coal in any given reaction (combustion, pyrolysis, gasification, liquefaction, etc.) will differ from those of another coal under similar circumstances. It is even impractical to operate some processes with certain coals (e.g., coking with lignite or CO_2 Acceptor gasification with bituminous coals). Despite the extreme variability, it is possible to generalize about coal and coal reactions, providing that the limitations are kept in mind.

Coal Gasification

Gasification of coal transforms a cumbersome, inconvenient, dirty solid fuel into a convenient, clean, gaseous fuel, or into synthesis gas. The impetus for this effort is that both the individual consumer and business have become highly dependent upon natural gas. At the same time the rate of natural gas production is and has been exceeding the rate at which new gas reservoirs are being discovered and added to the supply system. Alternately our coal reserves are sufficient for approximately 300 years at the accelerated production rates proposed in the recent national energy initiatives.

Gasification of coal entails the treatment of coal in a reducing atmosphere with air, oxygen, steam, CO_2, or hydrogen or mixtures of these gases, to yield a combustible product. The product of primary gasification of coal and of the reaction of coal carbon with the gasifying agent is usually a mixture of H_2, H_2O, CO, CO_2, CH_4, inerts (such as nitrogen), and minor amounts of hydrocarbons and other impurities.

The product is called a low-Btu gas if an air-steam mixture is used directly to gasify the coal and it contains nitrogen as a major component. Low-Btu gas is suitable for use as an energy source near its point of generation, but, because of its low Btu content, it is not economically attractive for long distance transmission.

Intermediate-Btu gas (synthesis gas), which contains only a minor amount of nitrogen, is obtained when oxygen-steam mixtures are used to gasify the coal. Intermediate-Btu gas can be used either as an energy source or as a synthesis gas for the production of chemicals and synthetic liquid and gaseous fuels.

Table 1. Mean analytical values for 101 bituminous coals.[a]

Constituent	Mean	Standard Deviation	Minimum	Maximum
Arsenic	14.02 ppm	17.70	0.50	93.00
Boron	102.21 ppm	54.65	5.00	224.00
Beryllium	1.61 ppm	0.82	0.20	4.00
Bromine	15.42 ppm	5.92	4.00	52.00
Cadmium	2.52 ppm	7.60	0.10	65.00
Cobalt	9.57 ppm	7.26	1.00	43.00
Chromium	13.75 ppm	7.26	4.00	54.00
Copper	15.16 ppm	8.12	5.00	61.00
Fluorine	60.94 ppm	20.99	25.00	143.00
Gallium	3.12 ppm	1.06	1.10	7.50
Germanium	6.59 ppm	6.71	1.00	43.00
Mercury	0.20 ppm	0.20	0.02	1.60
Manganese	49.40 ppm	40.15	6.00	181.00
Molybdenum	7.54 ppm	5.96	1.00	30.00
Nickel	21.07 ppm	12.35	3.00	80.00
Palladium	71.10 ppm	72.81	5.00	400.00
Lead	34.78 ppm	43.69	4.00	218.00
Antimony	1.26 ppm	1.32	0.20	8.90
Selenium	2.08 ppm	1.10	0.45	7.70
Tin	4.79 ppm	6.15	1.00	51.00
Vanadium	32.71 ppm	12.03	11.00	78.00
Zinc	272.29 ppm	694.23	6.00	5,350.00
Zirconium	72.46 ppm	57.78	8.00	133.00
Aluminum	1.29 %	0.45	0.43	3.04
Calcium	0.77 %	0.55	0.05	2.67
Chlorine	0.14 %	0.14	0.01	0.54
Iron	1.92 %	0.79	0.34	4.32
Potassium	0.16 %	0.06	0.02	0.43
Magnesium	0.05 %	0.04	0.01	0.25
Sodium	0.05 %	0.04	0.00	0.20
Silicon	2.49 %	0.80	0.58	6.09
Titanium	0.07 %	0.02	0.02	0.15
Organic Sulfur	1.41 %	0.65	0.31	3.09
Pyritic Sulfur	1.76 %	0.86	0.06	3.78
Sulfate Sulfur	0.10 %	0.19	0.01	1.06
Total Sulfur	3.27 %	1.35	0.42	6.47
Moisture	9.05 %	5.05	0.01	20.70
Volatile Matter	39.70 %	4.27	18.90	52.70
Fixed Carbon	48.82 %	4.95	34.60	65.40
Ash	11.44 %	2.89	2.20	25.80
Btu/lb	12,748	464.50	11,562.00	14,362.00
Carbon	70.28 %	3.87	55.23	80.14
Hydrogen	4.95 %	0.31	4.03	5.79
Nitrogen	1.30 %	0.22	0.78	1.84
Oxygen	8.68 %	2.44	4.15	16.03
High-Temperature Ash	11.41 %	2.95	3.28	25.85
Low-Temperature Ash	15.28 %	4.04	3.82	31.70

[a] Adapted from the work of Ruch et al. (1974)

Synthetic pipeline gas, which is indistinguishable from natural gas and contains over 90 percent CH_4, is produced by further processing of intermediate-Btu gas. The required processing includes removal of particulate matter and condensables, adjustment of the gas composition by converting some of the CO to H_2 and CO_2 (shift conversion), removal of H_2S and CO_2, and methanation of the resulting gas mixture.

The pyrolysis or devolatilization of coal to char and volatile matter occurs during coal heating.

1. $\text{Coal} + \text{heat} \longrightarrow C + \text{volatile hydrocarbons}$

The gasification of char with CO_2,

2. $C + CO_2 \longrightarrow 2\,CO$

and the water-gas shift or hydrogasification reaction

3. $C + H_2O \longrightarrow CO + H_2$

are the heart of the gasification reaction and supply the synthesis gas. The hydrogasification reaction and the gasification of char with CO_2

4. $C + CO_2 \longrightarrow 2\,CO$

are slow and are thermodynamically favored at temperatures above 1350°F (732°C), but are rarely at equilibrium at temperatures below 2000°F (1093°C). Heat for this reaction is supplied by the combustion reactions

5. $C + \frac{1}{2}\,O_2 \longrightarrow CO$

6. $C + O_2 \longrightarrow CO_2$

7. $H + \frac{1}{2}\,O_2 \longrightarrow H_2O$

which are very rapid and proceed to completion with oxygen disappearance. The methanation of char

8. $C + 2\,H_2 \longrightarrow CH_4$

is highly exothermic and is thermodynamically favored at high pressure or at temperatures less than 1150°F (621°C). The shift reaction

9. $CO + H_2O \longrightarrow CO_2 + H_2$

is mildly exothermic and because it has a favorable equilibrium at temperatures below 1350°F (732°C), it is usually carried out externally to the reactor. The methanation reaction

10. $CO + 3\,H_2 \longrightarrow CH_4$

is highly exothermic but is favored at low temperatures and elevated pressures. This reaction, necessary to the production of pipeline quality gas, is generally catalytically augmented and is carried out externally to the reactor.

Because any incremental increase in methane production (reactions 8 and 10) in the gasifier favors the economics of pipeline gas production, most high-Btu gasification processes are high-pressure processes. For the same reason, several of the advanced or second generation coal gasification processes (processes not already commercialized) utilize a hydrogen gas feed to augment or replace that produced by the water-gas shift reaction. Alternately, methane content is not of economical significance in low-Btu coal gasification and these processes tend to favor low pressure.

Coal Gasification Research Facilities

Coal gasification research facilities include low- and medium- as well as high-Btu gasification processes. From a number of coal gasification projects currently planned or under way (Table 2), seven were chosen (Table 3) from which to generalize about all such plants. Each is currently investigating a unique feature of the gasification process, as illustrated in the following list of plants chosen and their special focuses:

HYGAS — Two-stage hydrogasification plus one-stage standard gasification utilizing counter-current flow of solids and gas

CO_2 Acceptor — Utilization of chemical reaction between CaO and CO_2 to supply process heat and to drive the gasification reaction to high hydrogen production rates with lignite

Synthane — Utilization of any coal for the production of natural gas via simplified pretreatment plus fluid-bed gasification

Bi-Gas — Utilization of medium-temperature dilute-phase gasification followed by high-temperature combustion to produce a synthetic natural gas from any coal

MERC — Demonstration of the direct use of fixed-bed processes with fine and/or agglomerating coals

Agglomerating Burner — Production of high-Btu gas from caking coals with air by using agglomerated ash as a heat transfer mechanism

Steam-Iron — Production of hydrogen from coal char utilizing the oxidation of iron powder and reduction of iron oxide

The seventh process described above utilizes char, rather than coal, as its feed material to produce hydrogen for hydrogasification or hydroliquefaction processes, including HYGAS, Hydrane, Solvent Refined Coal, and H-Coal. As such, the Steam-Iron process may be an integral part of the gasification process and was chosen for study as an example of processes that might utilize char in noncombustion processes.

Table 2. Second generation coal gasification processes under consideration.

Developer	System	Feed Requirement		Type of Process		Operating Pressure, psi	Operating Temperature, °F	Stage Development
		Size	Coal Restrictions	Reactor	Feed			
Westinghouse[a]	Combined Cycle	1/4" x 0	Dried	Fluidized bed surrounding central draft tube (feed) atop combustor	Steam, air	200	2100	Pilot
B&W[a]	Entrained bed	1/4" x 0	ND[b]	Pressurized, water-cooled gasifier	Air	50-100	Gasifier: 900 Combustor: 1600 at 95 psi	Pilot
Exxon[a]	Catalytic gasification	1/4" x 0	ND	Fluidized bed	Steam, air	Atmos-1000	Gasifier: 1400-1500 Char heater: 1700+	ND
Combustion Engineering[a]	Entrainment gasification	1/4" x 0	ND	Slagging, fixed bed	Steam, air	Atmospheric	Combustor: 3000-3200 Reductor: 3000-1780	Pilot
Grand Forks Energy Research Center[c]	Slagging Lurgi	Lump	Dried	Slagging, entrained bed	Steam, O_2	80-400	250-2800	PDU[d]
IGT[a]	U-Gas	1/4" x 0	Noncaking or pretreated caking (?)	Fluidized bed	Steam, air or Steam, O_2	Atmos-350	1900	PDU[d]
General Electric[a]	GE-Gas	ND	Noncaking or mildly caking	Moving fixed bed	ND	Atmos-250	250-1600	PDU[d]
ERDA[a]	Hydrane	Crushed	No pretreatment of bituminous coal necessary	2-zone hydrogen	Steam, O_2	1000	1650	Bench
M. W. Kellogg Company[a]	Molten salt	-12 mesh	None	Molten Na_2CO_3	Steam, air	420	1830	Bench
FMC[a]	Cogas	ND	Sub-bituminous and bituminous	Fluidized bed	Steam, air	50	1000	Pilot
AM Squires, CUNY[e]	Circulating bed	Crushed	ND	High velocity (10-40 ft/sec)	Steam, air or O_2	ND	2200-2300	Bench (at HRI)
University of Wyoming[a]	Multiple catalyst	ND	ND	Heated Ni catalyst	Steam	1000	1200-1300	Bench
Foster Wheeler[a]	Entrained feed	ND	ND	Entrained-type, 2 stage slagging pressure gasifier	Steam, air	520	2100+	ND
	(Nuclear process heat)[f]	ND	Dried	Heated He from nuclear plant provides heat for coal hydrogasification	ND	560-1400	1550-1630	Paper

[a] Adapted from the work of Howard-Smith and Werner (1976).
[b] No data.
[c] Adapted from the work of Ellman and Johnson (1976).
[d] Process development unit.
[e] Adapted from the work of Squires (1976).
[f] Adapted from the work of Schrader et al. (1975).

Table 3. Coal gasification systems used as references.

Process	Pressure, psig	Temperature, °F	Product		Coal Feed	Status (Dec. 1976)	Type
			Gas Quality	Liquids			
HYGAS, Steam-Oxygen	1000^a $1000\text{-}1500^c$	1300-1900	Medium or high	Light oil and tar	Lignite Sub-bituminous Bituminous[b]	Operational	Pilot
CO_2 Acceptor	150^a $150\text{-}300^c$	$1500\text{-}1850^d$	Medium or high	None	Lignite Sub-bituminous	Operational	Pilot
MERC Unit	200^a $\text{Atmos-}300^c$	Combustion zone 2400-2500 Gas off take 1000-1200	Low, medium, or high	Light oil and tar	Lignite Sub-bituminous Bituminous	Operational	Pilot
Synthane	1000^a $600\text{-}1000^c$	1500^a $1400\text{-}1800^c$	Medium or high[e]	Light oil and tar	Lignite Sub-bituminous Bituminous[b]	Start-up	Pilot
Bi-Gas	Upper stage (entrained flow) 1000-1500 Lower stage (vortex flow) 1000-1500	1400-1700 2800	Medium or high[e]	(Doubtful)	Lignite Sub-bituminous Bituminous	Start-up	Pilot
Agglomerating Burner	Atmos-100	1800	Medium or high	(Questionable)	Lignite Sub-bituminous Bituminous[b]	Start-up	PDU
Steam-Iron	1000-1200	Hydrogasifier 1300-1700 Producer 2000-3000	Hydrogen	None	Char	Under construction	Pilot

[a] Normal operating pressure.
[b] Must pretreat agglomerating bituminous coal.
[c] Optimal range.
[d] Coal bed 1500°F, regenerator 1840°F.
[e] Can be converted to low-Btu gas production.

In addition to the unique feature of each gasification process, each pilot plant is also a test bed for process equipment such as pumps, valves, insulation, repair techniques, and metallurgy, and for downstream techniques such as quenching, acid gas scrubbing, methanation, and sulfur removal. Despite the differences introduced by this variety of research goals, the unit operations of most pilot plants are quite similar (Table 4). The same is true of their operating and maintenance techniques. Further, the primary process streams, while differing in quality, are sufficiently similar in their major constituents (Table 5) that generalization about major properties for the purpose of this document will not produce major discrepancies. However, generalization about minor constituents in the process streams is most difficult since the exact constitution of the process streams is not yet known in detail (Magee et al. 1973), and concentrations of minor constituents change depending upon reactor configuration, residence time, reaction temperature or reaction-temperature sequence, pressure, and coal feed (Braunstein 1976). This second point must be emphasized: The composition of the "oil" and tar products from any given reactor may be unique to that process. One example is the difference between the condensable oils found in the off-gas from HYGAS and the expected condensable oils in the Synthane off-gas. Oil from HYGAS is 85% toluene, 8% benzene, and 3% C_9 aromatic hydrocarbons (Lee 1975). In contrast, based on laboratory data, little minus 100°C oil (benzene) is anticipated from Synthane (oral communication December 9, 1976, by A. J. Forney, Pittsburgh Energy Research Center, Bruceton, Pennsylvania) and 30% to 60% of the oil product is expected to have a boiling point in excess of 500°C (932°F) (Forney et al. 1974). Unlike liquefaction or pyrolysis processes (coking), gasification processes provide — through the carbon-steam reaction — atmospheres containing relatively large quantities of hydrogen, so that gasification products are not necessarily the same as liquefaction or pyrolysis products. The fact that some compounds are formed commonly by all three reactions (gasification, pyrolysis, liquefaction) does not give one license to assume that all substances found in one operation will be found in all operations. As the data indicate, the range of *known* second generation gasification products is limited. Known plus suspected gasification products are shown in Appendix A.

The Synthane Pilot Plant (Figure 2) has been chosen for the generalized process description which follows. This process was chosen because of its relative simplicity, because it contains more points of similarity to the gasification pilot plants referred to here than any other process, and because of the variety of products anticipated from this plant. Information from or pertaining to the remaining six processes will be used to illustrate, or be presented as, special cases.

SOLIDS HANDLING

Coal Storage

The coal or char storage piles in coal gasification pilot plants tend to be relatively small, varying from no storage to several railroad carloads. Coal is either taken from the storage piles with a front-end loader (e.g., at the HYGAS and Agglomerating Burner plants) or unloaded from a truck or railroad car to an underground storage bin. From this bin, it is transported by conveyor belt to a closed tank (e.g., at the CO_2 Acceptor, Bi-Gas, and Synthane plants).

Table 4. A synopsis of unit operations at seven coal gasification research facilities.

Unit Operation	HYGAS	CO_2 Acceptor	MERC Unit	Synthane	Bi-Gas	Agglomerating Burner
Coal stock pile	Yes	Stored offsite	Yes	Stored off site	Yes — compacted	Yes
Coal feed	Payloader-bin-conveyor	Truck-bin-conveyor	Truck-bin-conveyor	Truck or railroad-bin-conveyor	Truck or railroad-bin conveyor	Payloader-bin-screen to -35 mesh
Coal preparation	Williams mill (negative pressure) water scrub	Williams mill (positive pressure) water scrub	Run of mine steam dry	Dryer, Raymond mill, screen	Cage mill wet ball mill	Williams mill
Ground coal storage	Purged bin	Purged bin	Bin	Purged bin	Purged bin	Purged bin
Gasifier feed	Toluene slurry	Simple lockhopper	Simple lockhopper	Petrocarb lockhopper	Water slurry steam-injected	Lockhopper
Pretreatment	Low pressure	No	No	High pressure	No	Low pressure, if required
Gasification	Countercurrent flow through fluid beds	Dolomite plus char fluid beds	Stirred fixed bed	Single fluid bed	Medium-and high-temperature entrained beds	Agglomerated ash supplies gasification heat to fluid bed
Gas quench	Quench towers	Water venturi	Cyclone separator	Water-venturi	Water-venturi	Water-venturi
Gas scrubbing	Water	Water	No	Water, then oil	Water	No
Shift	No	No	No	Fixed bed	Fixed bed	No
Acid gas scrub	Diglycolamine	Hot carbonate	No	Benfield	Selexol	No
Methanation	Ni catalyst cold gas recycle	Packed tube reactor	No	Tube-wall reactor (Raney Ni)	Fluidized bed to fixed bed	No
Gas product disposal	Thermal oxidation	Thermal oxidation	Thermal oxidation	Thermal oxidation	Thermal oxidation	Thermal oxidation
Sulfur	Claus	Thermal oxidation	Thermal oxidation	Stretford	Claus	Thermal oxidation
Water	Filter, city sewage disposal	Hay filter, city sewage disposal	Thermal oxidation	Thermal oxidation	Filter, city sewage disposal	Thermal oxidation
Condensable hydrocarbons	Recycle	None	Thermal oxidation	Thermal oxidation	Tar generation not expected	Thermal oxidation
Ash or Char	Filtered and disposed	Dredged from pond	Disposal	Filtered and disposed	Slag from lower stage is water-quenched	Landfill
Overhead coal or char	Filtered and disposed	Sent to pond to settle for later disposal	Thermal oxidation	Thermal oxidation	Pond for later disposal	Thermal oxidation

Table 5. Gasifier products.

Product	HYGAS[a,b]	CO_2 Acceptor[c]	MERC Unit[d]	Synthane[e]	Bi-Gas[f,g]	Agglomerating Burner[h]	Steam-Iron[i]
Coal Feed Rate (lb/hr)	6000	2730	2250	2000-6000	10,000	1225	ND[j]
Gasifier Overhead Products (vol %)							
Carbon Dioxide	4.8	6.6	9.6	18.3	16.2	5.6	0.0
Carbon Monoxide	9.7	8.7	16.6	7.9	22.1	27.0	0.0
Hydrogen	33.1	38.8	16.9	12.3	24.2	49.7	26.0
Methane	19.0	9.0	2.4	11.9	11.8	ND	0.0
Ethane	ND	ND	0.2	0.4	ND	ND	0.0
Water	31.8	34.7	8.3	46.8	24.6	17.0	73.4
Nitrogen	0.4	2.2	45.5	0.9	0.5	0.3	0.6
Ammonia	ND	ND	ND	0.7	ND	ND	0.0
Oil and Tar	0.6[k]	0.0	ND	0.4	ND	ND	0.0
Hydrogen Sulfide	0.6	0.05	0.5	0.4	0.6	0.4	0.0
Solids (char or coal)	5%-10% coal feed	105 lb/hr	2%-4% coal feed	5%-10% coal feed	ND	5%-10% coal feed	ND

[a] Adapted from the work of IGT (1973).

[b] Adapted from the work of Anastasia and Blair (1975).

[c] Adapted from the work of Stearns-Roger (1976b).

[d] Adapted from the work of Lewis et al. (1975).

[e] Adapted from the work of Haynes and Forney (1972).

[f] Adapted from the work of Grace and Diehl (1974).

[g] Adapted from the work of Grace (1972).

[h] Adapted from the work of Battelle Columbus Laboratories (1974).

[i] Adapted from the work of Detman (1976).

[j] No data.

[k] Does not include slurry oils.

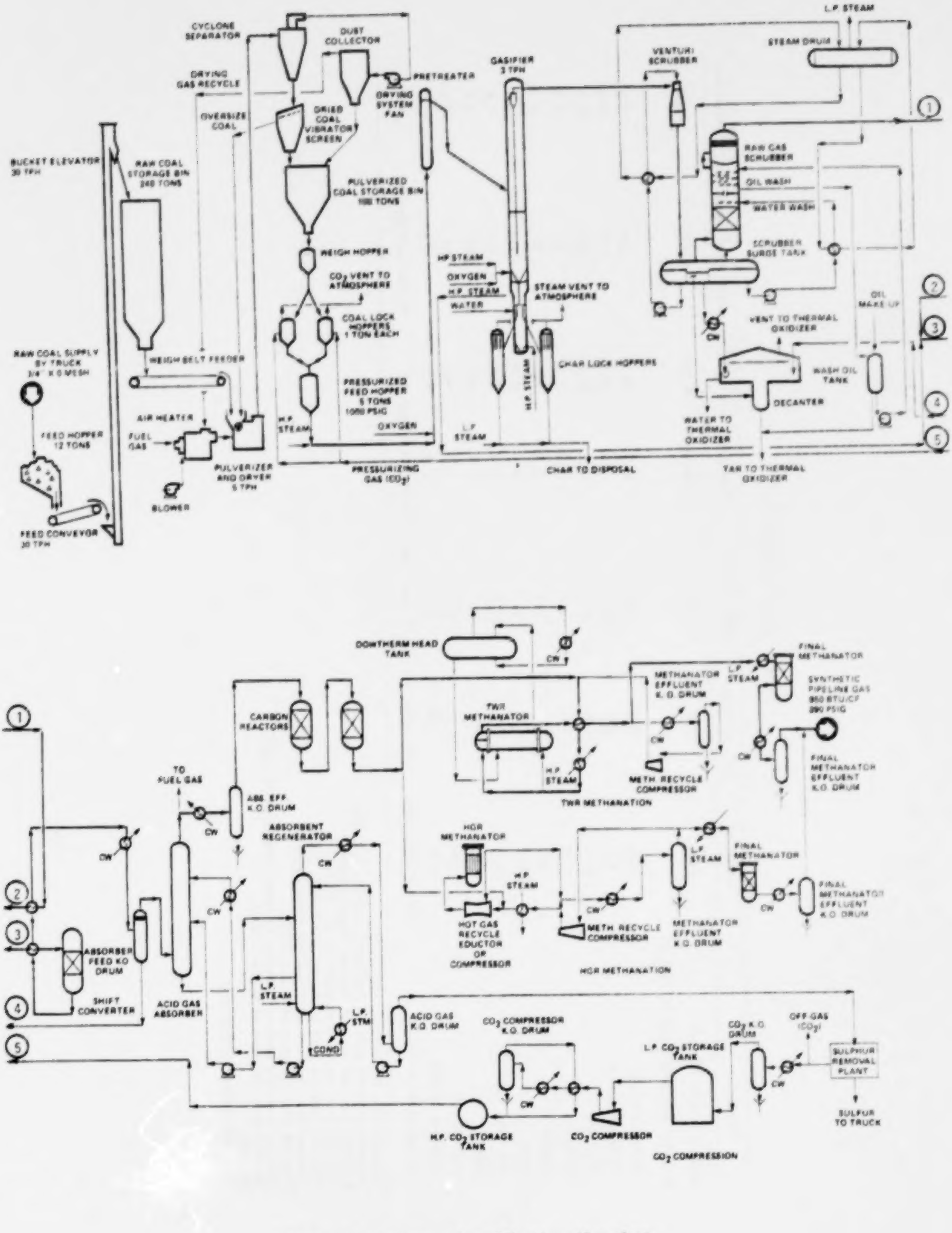
CYCLONE SEPARATOR
DUST COLLECTOR
DRYING GAS RECYCLE
PRETREATER
DRYING SYSTEM FAN
OVERSIZE COAL
DRIED COAL VIBRATORY SCREEN
BUCKET ELEVATOR 30 TPH
RAW COAL STORAGE BIN 240 TONS
PULVERIZED COAL STORAGE BIN 100 TONS
WEIGH HOPPER
CO_2 VENT TO ATMOSPHERE
COAL LOCK HOPPERS 1 TON EACH
RAW COAL SUPPLY BY TRUCK 3/4" X 0 MESH
WEIGH BELT FEEDER
PRESSURIZED FEED HOPPER 5 TONS 1000 PSIG
AIR HEATER
FUEL GAS
FEED HOPPER 12 TONS
H.P. STEAM
OXYGEN
PULVERIZER AND DRYER 5 TPH
PRESSURIZING GAS (CO_2)
BLOWER
FEED CONVEYOR 30 TPH
GASIFIER 3 TPH
VENTURI SCRUBBER
L.P. STEAM
STEAM DRUM
①
RAW GAS SCRUBBER
OIL WASH
WATER WASH
SCRUBBER SURGE TANK
HP STEAM
OXYGEN
H.P. STEAM
WATER
STEAM VENT TO ATMOSPHERE
CHAR LOCK HOPPERS
HP STEAM
CW
VENT TO THERMAL OXIDIZER
②
OIL MAKE UP
③
WASH OIL TANK
DECANTER
④
L.P. STEAM
WATER TO THERMAL OXIDIZER
⑤
CHAR TO DISPOSAL
TAR TO THERMAL OXIDIZER
DOWTHERM HEAD TANK
CW
FINAL METHANATOR
L.P. STEAM
METHANATOR EFFLUENT K.O. DRUM
SYNTHETIC PIPELINE GAS 950 BTU/CF 990 PSIG
CARBON REACTORS
TWR METHANATOR
CW
H.P. STEAM
METH. RECYCLE COMPRESSOR
FINAL METHANATOR EFFLUENT K.O. DRUM
TWR METHANATION
TO FUEL GAS
ABS. EFF. K.O. DRUM
CW
ABSORBENT REGENERATOR
HGR METHANATOR
L.P. STEAM
FINAL METHANATOR
H.P. STEAM
FINAL METHANATOR EFFLUENT K.O. DRUM
HOT GAS RECYCLE EDUCTOR OR COMPRESSOR
METH. RECYCLE COMPRESSOR
METHANATOR EFFLUENT K.O. DRUM
HGR METHANATION
ABSORBER FEED KO DRUM
SHIFT CONVERTER
ACID GAS ABSORBER
L.P. STEAM
L.P. STM
COND
ACID GAS K.O. DRUM
CO_2 COMPRESSOR K.O. DRUM
CO_2 K.O. DRUM
OFF GAS (CO_2)
L.P. CO_2 STORAGE TANK
SULPHUR REMOVAL PLANT
H.P. CO_2 STORAGE TANK
CO_2 COMPRESSOR
SULFUR TO TRUCK
CO_2 COMPRESSION

Figure 2. Synthane coal gasification pilot plant.

Problems--
There are three types of health and safety problems associated with this initial coal storage and transportation sequence: dusting, fire, and leaching.

Dusting--The greatest amount of dust will be generated when a truck or railroad car is unloaded. (If the coal is unloaded into a bin [CO_2 Acceptor] and the bin is enclosed on three sides, as is done at many coal mines, spread of the dust into the surrounding area will be reduced.) Coal dust can and will blow off of a storage pile or conveyor. Coal will also be scattered and crushed when a front-end loader is used to convey coal from a concrete pad to a bin (HYGAS, Agglomerating Burner). There are no means of alleviating this problem. In passing from the receiving bin to the storage bin, coal is fed into a moving belt with a vibrating conveyor, then passed under a magnet which removes scrap iron, and finally to a bucket elevator. At each transfer point the coal can and will produce more dust.

Observation of existing coal gasification pilot plants both during operation and when shut down has indicated that coal pile and conveyor dusting should normally be only a nuisance to plant operators and a housekeeping problem. In general, gasification workers do not appear to be at risk from coal dust. The possible exceptions are those personnel assigned to unloading, front-end loader operation, or cleanup (all of these jobs are intermittent).

Fire--Coal will ignite spontaneously under at least two conditions:

1) Lignite or sub-bituminous coals will ignite when dried and exposed to air at ambient conditions. Resultant fires tend to be on the surface.

2) High-sulfur bituminous coals, especially coals containing fines, will ignite after excessive exposure to normal weather. Such fires are not uncommon after 2 to 6 months of exposure. Fires in these coals tend to be submerged in the piles. Small piles of "fine" high-sulfur bituminous coal dust, such as might accumulate from dusting or equipment leakage, may ignite within 12 to 48 hours, according to M. A. Evans (oral communication December 2, 1976, 620 N. Franklin Street, Somerset, Pa.).

Fires in the small coal storage piles normally found at pilot plants should pose few or no safety problems because of the size of the piles and the relative frequency of inventory turnover. (This is especially true where good housekeeping practices are followed.) However, the hazardous gases, vapors, and particulates from such a fire would be similar to those found in coke oven emissions or in other destructive distillation processes.

Leaching--Coal exposed to rain will be subjected to leaching by the water. Water will also carry coal fines into the plant sewer system, and in many cases this water may go into the plant water treatment pond.

Currently very little is known about the effect of residence time, weather, pile size, and coal composition of the leachate from coal storage piles. Several long-term (5-year) studies are being considered by both the Bureau of Mines and the Illinois State Geological Survey (oral communication, February 1976, with H. J. Gloskoter, Illinois State Geological Survey, Urbana, Illinois). One piece of information that has recently become available is presented in Table 6, which does indicate that a number of objectionable compounds can be dissolved. Even this limited information indicates that the concentration of dissolved materials in the leachate varies widely. Unfortunately, the table includes no data on either coal composition or other factors mentioned.

Coal Preparation

The raw coal from storage must be properly sized and dried before it is fed to the gasifier system (Figure 3). The coal is passed through a presizing crushing operation (a hammermill is generally used) to eliminate large lumps. The coal is then fed directly to a mill, where it is crushed and dried simultaneously. (Williams mills are used at CO_2 Acceptor [positive pressure], HYGAS [negative pressure], and Agglomerating Burner plants; a ball mill is used at the Bi-Gas plant; and a Raymond mill is used at the Synthane plant.) A mixture of hot flue gas from an auxiliary furnace and recycle gas is also piped into the mill at such a quantity and velocity that the ground coal is conveyed pneumatically to a cyclone located at the top of the structure, and the coal is simultaneously dried. Gas temperatures at the cyclone vary from 175° to 350°F (79° to 177°C) depending upon the rank of the coal being ground. Gas composition includes only minimal quantities of oxygen (which are defined by rank of coal being ground, fineness of grind, drying gas temperature, and mill system being used). The CO_2 Acceptor plant limits oxygen concentration to 3 to 5 vol % while other units grinding Eastern bituminous coal to -14 mesh and drying it at 180°F (82°C) find that 15 vol % oxygen is below the explosive limit. (Mill systems are generally equipped with oxygen monitors, auxiliary inert gas feed systems, and blowout hatches.)

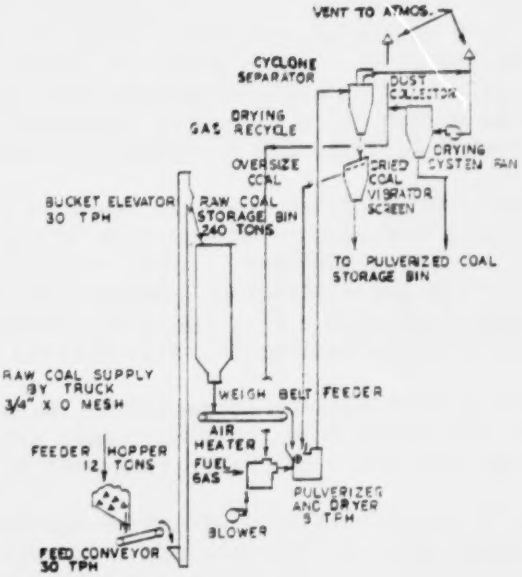
VENT TO ATMOS.
CYCLONE SEPARATOR
DUST COLLECTOR
DRYING GAS RECYCLE
DRYING SYSTEM FAN
OVERSIZE COAL
DRIED COAL VIBRATOR SCREEN
BUCKET ELEVATOR 30 TPH
RAW COAL STORAGE BIN 240 TONS
TO PULVERIZED COAL STORAGE BIN
RAW COAL SUPPLY BY TRUCK 3/4" X 0 MESH
WEIGH BELT FEEDER
AIR HEATER
FEEDER
HOPPER 12 TONS
FUEL GAS
PULVERIZER AND DRYER 5 TPH
BLOWER
FEED CONVEYOR 30 TPH

Figure 3. Synthane coal gasification process (coal preparation).

Table 6. Analyses of drainage from two industrial coal piles.[a]

Constituents	Concentration, mg/liter	
	Plant J	Plant L
Acidity (total), as $CaCO_3$	1,700	270
Calcium	240	350
Chemical oxygen demand	9	ND[b]
Chloride	0	ND
Conductance, mho/cm	2,400	2,100
Dissolved solids (total)	3,200	1,500
Hardness, as $CaCO_3$	600	980
Magnesium	1.2	0.023
pH, unit	2.9	2.9
Potassium	ND	0.5
Silicon (dissolved)	91	ND
Sodium	ND	4.1
Sulfate	2,600	ND
Suspended solids (total)	550	810
Turbidity, JTU	300	ND
Aluminum	190	ND
Arsenic	0.01	0.009
Barium	ND	0.1
Beryllium	ND	<0.01
Cadmium	<0.001	<0.006
Chromium	<0.005	<0.005
Copper	0.56	0.18
Iron	510	830
Lead	<0.01	0.023
Manganese	27	110
Mercury	<0.0002	0.027
Nickel	1.7	0.32
Selenium	0.03	0.003
Titanium	<1	ND
Zinc	3.7	1.0

[a] From the work of Chu et al. (1976).
[b] No data.

Coal from the cyclone passes over a vibrating screen that returns oversize material to the mill, while undersize material is conveyed by gravity or screw conveyor to a fine-coal bin. The fine-coal bin is airtight and it is purged with inert gas to prevent fires, explosions, and moisture pickup by the coal.

The fine coal is removed from the cyclone discharge gas; a portion of the gas is recycled to the furnace; and a smaller portion of the gas is purged from the system to the atmosphere to reduce the gas moisture content. Both the baghouse system and the venturi water scrubbing system have been used to remove the fine coal from the cyclone discharge gas. The venturi has become the more popular for pilot plant operation because of the number of problems encountered with the baghouse. Either system can produce a discharge gas of acceptable quality. Fines from the baghouse are discharged to the fine-coal bin. Fines accumulated in the circulating water of the venturi scrubber are discharged to the dirty water pond at a concentration of approximately 5 wt % solids.

Problems--
In coal crushing sections of the plant, there tend to be two types of problems, other than those already discussed.

Dusting--Dusting may present an inhalation hazard with the potential for precipitating pneumoconiosis. (Casarett and Doull [1975] linked respirable coal dust to pneumoconiosis [black lung]). Dusting is also a safety hazard; both from the very real potential for dust explosion, which increases with decreasing coal rank, and as a fire hazard under the conditions already described. Dusting from any equipment is possible, particularly if the equipment has to be maintained often and is not properly reassembled. (Elevators, rotating valves [star valves], augers or conveyors, and vibrating screens are common points of rapid wear and failure.)

Dusting during plant operation is, in general, not a major problem, provided that good housekeeping and maintenance procedures are consistently followed. Dusting can be a major problem when equipment or bins must be maintained or emptied inasmuch as pilot plants may not have facilities for the removal of coal from bins. This can be a very dusty and dirty procedure. (Fortunately, it is not often necessary.)

Noise--All grinding operations are inherently noisy. Screening operations are also noisy, although vibrating screens in most pilot plants are located away from normal traffic.

Special Cases--Two of the pilot plants use other feed solids in addition to coal. The CO_2 Acceptor operation crushes and screens dolomite or limestone to a 6 by 8 mesh particle size, while the Bi-Gas plant is prepared to add finely crushed silica or limestone to the feed to alter the coal ash slagging properties as required. In either case, the problems are similar to those encountered with coal, except that fires and explosions would not be anticipated.

At the Bi-Gas plant, coal is fed into a cage mill for initial grinding. Upon demand, the cage mill product is mixed with water and final pulverization is accomplished in a wet ball mill. The ball mill product is sent to a weigh tank (Grace and Diehl 1974).

Coal Feeding

Coal is fed from the pulverized coal storage bin through a lockhopper system to the gasifier. The Synthane Pilot Plant uses a Petrocarb lockhopper system (Figure 4), which operates as follows: Pulverized coal flows from the coal storage bin through two low-pressure valves to a weigh-hopper. When the 0.85-ton weigh-hopper is filled, a low-pressure diversion valve is opened below the weigh-hopper and two high-pressure valves above the storage injector are opened. The 0.85-ton storage injector is filled and all valves are closed. The injector is pressurized with inert gas (CO_2) to 1065 psig. Two high-pressure valves below the storage injector are opened to the 5-ton primary injector and the coal flows by gravity into it. All valves are then closed. The inert gas from the storage injector is bled to the thermal oxidizer. The sequence is then repeated. The storage injector system is duplicated so that while one injector is filling, the other is discharging. The Synthane lockhopper system is the most sophisticated such system in operation at any pilot plant at this time. Others have less elaborate valving (single rather than double) and are more directly connected to the reactor (e.g., MERC, CO_2 Acceptor).

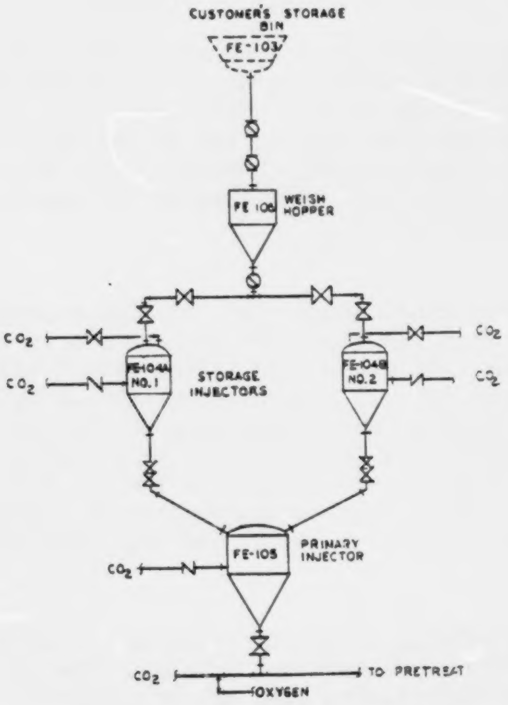

Figure 4. Petrocarb lockhopper system (Synthane Pilot Plant)[a]

[a]Petrocarb, Inc., (1975).

Problems--
The one primary problem in this area is lockhopper valves; a problem of lesser importance involves the cleaning and maintenance of these valves and vessels.

Lockhopper valves are subject to extraordinary abuse. They must hold a differential pressure of from several hundred to 1000 psig. At the same time, they must pass large quantities of solids rapidly and thus must be relatively large. Fine solids may adhere to the valve seating surfaces and invariably either the valve surface is abraded, or the valve cannot be closed against the solids. In either case, process gas may escape to the low-pressure portion of the system and then to the atmosphere. The composition of this escaping gas depends upon two factors:

- The proximity of the lockhopper to the reactor
- The reactor feed point (i.e., above the bed, into the bed, or at the bottom of the bed)

In the worst case, it may be assumed that the escaping gas will have the same composition as that of the off-gas from the reactor. The degree of seriousness obviously varies with the total system utilized. For example, in the Synthane plant, coal is carried pneumatically with steam to the pretreater. A leak in the Petrocarb valving system would consist of CO_2 or steam. The lockhopper system for the MERC unit is directly connected to the top of the fixed-bed reactor through a two-valve system. Leaking gas from the lockhoppers would contain reactor gasification products.

Should the valves leak process gas to the atmosphere, it is certain that portions of the hydrocarbon vapors contained in the gas would condense on the cold interior surfaces of the valves. They would also condense on interior vessel surfaces and on any feed coal in any of the vessels or piping through which they might pass. Hydrocarbon condensate would also be deposited around the exterior surfaces at the leak point and on any nearby structures, depending upon the size of the leak.

Special Cases--
Two of the pilot plants, HYGAS and Bi-Gas, utilize slurry feed systems. At the HYGAS plant, coal from the fine-coal storage bin is fed continuously into a slurry-mix weigh tank, which has been filled with light oil (∿ 86% toluene). The slurry is mixed both by a turbine blade mixer and by circulation from the bottom of the tank through a centrifugal pump to the top of the tank. When a run is started, circulation is diverted through a high-pressure piston pump (spared*). Excess slurry is recirculated to the mix tank. From the piston pump, the pressurized slurry flows at a velocity of approximately 6 ft/sec through a heater (temp = 300°F or 149°C) and then into the reactor.

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*A duplicate pump and valving system is installed in parallel so that either pump can be used. Should one pump malfunction, flow can be switched to the spare pump and the malfunctioning pump can be repaired.

The feed arrangement at the Bi-Gas plant is roughly similar, although water is used as the liquid carrier. Here the slurry from the piston pump passes through a preheater, where the water is flashed to steam. The coal is then transported pneumatically to a cyclone and into the gasifier.

A major problem with using a slurry feed system is one of housekeeping (leaking equipment). In the HYGAS Pilot Plant system, there is also the possibility of light hydrocarbon vapors' leaking from the slurry system. Pump problems are not uncommon, nor are plugged lines, especially during initial plant start-up.

Pretreatment

Background--

Many of the Eastern bituminous coals swell and melt as they are heated through the 400° to 800°F (204° to 427°C) range. As the particles melt, they adhere to one another. As the temperature is maintained or raised, the volatile constituents vaporize while the higher molecular weight liquids crack into light or vaporizable material and into unstable molecules that polymerize and "coke." This coking or agglomerating phenomenon is highly desirable for the making of coke but is undesirable in coal gasification, because, if coal agglomeration occurs in a fluid-bed gasifier, the fluid properties of the bed are destroyed, while in a fixed-bed gasifier an agglomerated bed would block the flow of air or oxygen through the bed.

The agglomerating properties of coal can be destroyed if the coal particles are exposed to a limited quantity of oxygen at approximately 800°F (427°C). Apparently, a thin layer of coal on the exterior of the particles combines with the oxygen, forming a surface film, which prevents particle agglomeration. During the pretreatment process, some off-gas is produced as indicated in Table 7. No data are available concerning the concentrations of sulfurous or nitrogenous gases from pretreatment or the exact analysis of the hydrocarbon vapors. Hydrocarbon vapor may be high in light oils content, but it will include a complete range of materials with boiling points up to the pretreating temperature (normally, 750° to 825°F [400° to 440°C]).

Operation--

In the Synthane process (see earlier section of this chapter on coal feeding), coal is metered out of the primary injector through a rotating valve to fall into a pickup pot. High-pressure steam from the utility section ($\sim$ 1100 psi, 556°F [291°C]) then transports the coal pneumatically to the pretreater. The transport line is electrically heated to initiate coal heat-up. Oxygen can also be supplied to the transport line to initiate pretreatment, if this is desirable.

It may be assumed that although the feed line is heated, the solids velocity will be sufficiently high to prevent pretreatment temperatures from being altered and that no pretreatment off-gases or hydrocarbon vapors are produced up to the pretreater feed inlet. Sufficient oxygen is added to the pretreater fluidizing gas to maintain the temperature at $\sim$ 800°F (427°C). Because of the circulation that exists in a fluid bed (discussed later in this chapter), it is again reasonable to assume that at least a portion of the pretreater off-gas, however diluted, exists at any given point within the pretreater. Both pretreater off-gases and pretreated coal are carried through the overflow pipe to the reactor.

Table 7. Coal pretreatment yields.

Test Number	F.B.P. 7[a]	F.B.I. 8[a]	Process Flow Diagram[b]
Coal	Pittsburgh	Illinois #6	Bituminous
Pressure, psi	1029	1029	Atmospheric
Temperature, °F (°C)			
Maximum	842 (450)	878 (470)	ND
Average	798 (426)	860 (460)	∿800 (427)
Residence Time, Min.	3	3	∿30
Pretreating gas: coal, wt ratio	1.07	1.01	0.76
O_2, vol, % pretreating gas	7	7	21
Steam : coal, wt ratio	0	0	0.47
Gas Yield			
scf/ton MAF[c] coal	1000	1140	3416
wt % of coal feed	5.1	5.1	15.3
Btu/lb coal	109.5	81.6	ND
Gas Analysis, vol %[d]			
H_2	2.1	2.8	ND
CO	8.4	8.4	44.4
CO_2	72.0	79.0	34.4
CH_4	16.5	8.8	}15.1
C_2H_6	1.0	1.0	
SO_2	ND	ND	6.1
Tar Recovered, lb/ton	20	42	16.4
Wt % Coal Feed	1.0	2.1	0.8

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[a] From the work of Gasior et al. (1976).
[b] From the work of Institute of Gas Technology (1973).
[c] Moisture-ash-free.
[d] O_2,N_2,H_2O free basis.

Special Cases--
In other pilot plants (HYGAS [Figure 5], Agglomerating Burner), pretreatment is carried out at essentially atmospheric pressure. The pretreatment mechanism is similar to that already described, except that raw coal may be fed with a screw conveyor directly to the pretreater fluid bed. The pretreated solids are removed from the bed by a fixed-point offtake or standpipe and, in general, are cooled before transfer to a holding bin. From here they are introduced into the gasifier feed system. The pretreater off-gases pass through a cyclone and are then scrubbed with a circulating water venturi scrubber. (This scrubber is similar to the gasifier off-gas scrubber described in detail later). The scrubbed gas is fed to the thermal oxidizer.

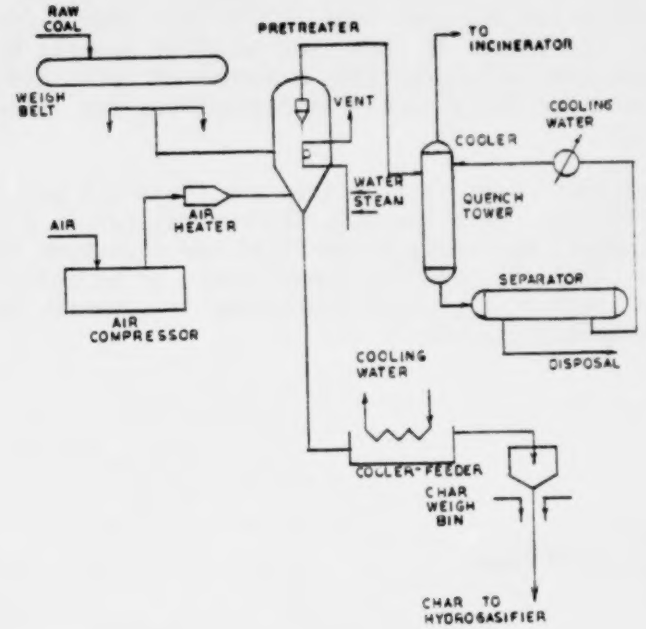
RAW COAL
PRETREATER
TO INCINERATOR
WEIGH BELT
VENT
COOLING WATER
COOLER
WATER
STEAM
QUENCH TOWER
AIR
AIR HEATER
SEPARATOR
AIR COMPRESSOR
DISPOSAL
COOLING WATER
COOLER-FEEDER
CHAR WEIGH BIN
CHAR TO HYDROGASIFIER

Figure 5. Coal pretreatment section, HYGAS start-up configuration.[a]
[a]Institute of Gas Technology (1975).

Problems--
It is important to note that any part of the pretreater or of the pretreater off-gas system may contain condensed aromatic hydrocarbon vapors. It is equally possible that the pretreated coal may contain condensed heavy tars. (At ambient temperatures, any such tars on or in the pretreated coal would be solids.) It is also possible that pretreater tars* contain compounds with

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*For the purpose of this document "tar" means condensable aromatic hydrocarbons.

boiling points in excess of the pretreater temperature of 800°F (420°C). These compounds would have melted at the pretreater temperatures and would therefore have exerted sufficient vapor pressure to be exhausted from the pretreater with the product gas.

GASIFIER

General

The gasifier is the heart of the coal gasification pilot plant operation. The pilot plant exists to study the process operating variables within this vessel. The gasifier may be 130 feet high and up to 5 feet in diameter. It may be built to operate at pressures below 100 psi (MERC, Agglomerating Burner) or at pressures of up to 1500 psi (Bi-Gas). It may be constructed to maintain temperatures which may vary from 1400°F to ∿ 3000°F (760°C to ∿ 1650°C). Further, the vessel is connected to other vessels by a number of major and minor lines and it incorporates a number of ports and hatches for use as inspection ports or for alternative connections for lines or instruments.

Six of the seven reactors under study either are fluid-bed units or have the fluid-bed characteristics. Only the MERC stirred reactor is a fixed-bed unit. The reactor vessel may contain one fluid bed (Synthane [Figure 6]), multiple fluid beds (HYGAS [Figure 7], Steam-Iron), or an entrained bed (Bi-Gas); or it may consist of several fluid beds in separate vessels (CO_2 Acceptor, Agglomerating Burner).

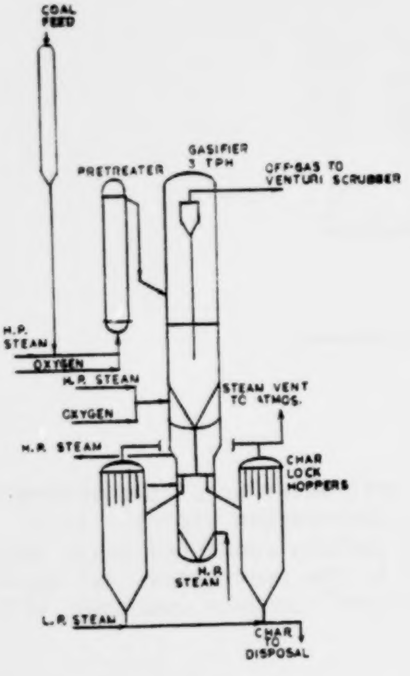
COAL FEED
PRETREATER
GASIFIER 3 TPH
OFF-GAS TO VENTURI SCRUBBER
H.P. STEAM
OXYGEN
H.P. STEAM
OXYGEN
STEAM VENT TO ATMOS.
H.P. STEAM
CHAR LOCK HOPPERS
H.P. STEAM
L.P. STEAM
CHAR TO DISPOSAL

Figure 6. Pretreater and gasifier — Synthane Pilot Plant.

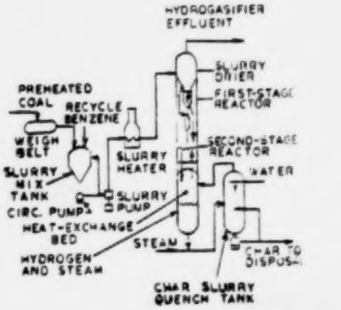
HYDROGASIFIER EFFLUENT
SLURRY DRIER
FIRST-STAGE REACTOR
PREHEATED COAL
RECYCLE BENZENE
WEIGH BELT
SECOND-STAGE REACTOR
SLURRY HEATER
WATER
SLURRY MIX TANK
SLURRY PUMP
CIRC. PUMPS
HEAT-EXCHANGE BED
STEAM
CHAR TO DISPOSAL
HYDROGEN AND STEAM
CHAR SLURRY QUENCH TANK

Figure 7. Hydrogasification reactor, start-up configuration[a] — HYGAS Pilot Plant.

[a]From: Schora (1975)

Two-Phase Fluidization--

As fluidization is a unit operation of major importance to most of the second generation coal gasification concepts, it will be defined in detail.

A fluidized bed consists of solids, which may be as large as 2½ inches or as small as 1 micron, although a bed of particles in the size range of 208 microns (65 mesh) to 12 microns is best for smooth operation. To fluidize these solids, gas is injected into the bottom of the bed in such a manner as to be evenly distributed over the bottom of the bed. When gas flow is initiated to the bed, the gas pressure increases until it equals the sum of the weight of the bed per unit of cross-sectional area plus the friction of the bed against the walls. When this point is reached the bed expands and the solids assume a more open arrangement, so that the gas can flow without exceeding the unit-bed weight. With further increases in gas velocity, the pores and channels enlarge and the particles become more widely separated. For free-flowing materials, the pore spaces eventually become so large that no stable arrangement can exist, and the particles will vibrate or circulate locally in a semistable arrangement; this is the point at which fluidization begins, forming the quiescent or incipient fluidized bed. Another increment of gas velocity results in overall circulation of the bed, often with transient gas streams flowing upward in channels that contain relatively few particles, with clumps or particles flowing downward (Perry et al. 1963). It is at this latter point that solids are carried from the dense phase (i.e., fluid bed) into the lean phase (disengaging space) of the reactor. While the heavier of these particles fall back into the bed relatively quickly, many are carried to the top of the reactor, where a cyclone is usually located. The cyclone will separate up to 99% of the particles from the gas entering it and will return them deep into the bed via the cyclone dipleg.

Advantages--

Fluid-bed processing offers several advantages over other modes of processing, such as fixed-bed. Fluidized beds are particularly adaptable to the contacting of free-flowing, nonsticky, granular solids with gases. Other advantages of fluid-bed systems include the following:

- Temperature Control

  1) Turbulence within the fluidized mass breaks up and disperses any hot or cold spots.

  2) High heat capacity of the bed stabilizes the temperature, permitting the bed to absorb large heat surges in the fluid with relatively small bed temperature changes.

  3) High heat-transfer rates are due to the large amount of transfer surface per unit volume of the bed. (The surface volume of ordinary sand would be 1000 to 5000 square feet/cubic foot of bed.)

- Continuity of Operation

  1) The high degree of internal turbulence and mixing assures rapid dispersal of fresh solids added to the bed.

2) Fluidized solids can easily be transported from vessel to vessel, and can be circulated in various paths at various densities and residence times through any network of processing equipment.

- Heat Transfer

  1) The fluid-bed offers the possibility of combining heat transfer with other operations.

  2) For large heat-transfer units, the fluid-bed equipment can be smaller than conventional heat-transfer equipment.

  3) Through the use of ceramic materials for interior wall construction, both corrosion and extreme temperature resistance can be easily obtained.

  4) Heat transfer can be effected in multiple stages, the fluidized solid acting as the heat reservoir to carry heat from one fluid to another; the stages may be physically close together.

  5) Heat transfer can be effected with extreme rapidity because of the large surface available — often with the ability to negate the unfavorable reactions that would occur at more leisurely heat-up rates.

  6) Similarly, a liquid may be heated, vaporized, and dispersed in a fraction of a second by direct contact with hot fluidized solids.

- Catalysis or Other Operations

  1) Easy control of bed or reaction temperature

  2) Maintenance of uniform catalyst activity

  3) Continuous removal of solid by-products

  4) Supply of heat to endothermic reactions

  5) Simple equipment with few moving parts

  6) Continuous operation with automatic controls

  7) Adaptability to sulfur scavenging via dolomite addition

Disadvantages--
Fluidized-bed systems also have disadvantages:

- Sticky or agglomerating solids cannot be processed.

- Fine solid particles may be formed, either trapped within the process or entrained in the gas leaving the bed.

- Particles are elutriated from the bed and carried along with the off-gas into the quench system, despite precautions.

- Solids withdrawn from the process are of average bed composition, thus making complete conversion in a single bed impossible.

- Localized overheating is possible if adequate gas dispersion is not provided.

- The pressure drop in the gas system of a fluidized-bed (boiling-bed) type of reactor is larger than in other types of equipment and may be a serious objection because of the large compressors required (Zenz and Othemer 1960).

Operation of Gasifiers

In general, raw or pretreated coal is injected into a gasifier either above the bed or into it. At the same time, fluidizing gas and/or steam and oxygen are fed to the bottom of the bed. Bed temperature is controlled for the needs and conditions of each reactor system. Ash or residual char is removed from the bottom of the bed and product gas is driven upward to the top of the reactor. Because in all cases the gas is carrying particles elutriated from the bed, it is passed through a cyclone. The solids escaping the cyclone are generally fine and may constitute as much as 1-5 wt % or even 10 wt % of the raw coal fed to the gasifier. In a free-fall injection system (Synthane, HYGAS), a major portion of the elutriated solids is coal. (Bi-Gas is a special case where it is desirable to have all solids elutriated from the bed.) In a bottom-of-the-bed coal injection system, the solid's composition will more closely approach that of the bed.

From the cyclone, the product gas leaves the reactor to be quenched. The line from the cyclone generally protrudes through the side or top of the reactor and is reasonably short, i.e., 10 to 20 feet at a maximum.

Gasifier Products

Because feed-entry geometry, temperature, pressure, and reactor configurations vary, it is difficult to define a generalized reactor product. This problem is complicated by the fact that few detailed studies have been made of the components produced in gasifiers. Undoubtedly there are significant differences in the gas-vapor composition at different levels within the reactor as the various dissociation, hydrogenation, polymerization, combustion, and reduction reactions occur. At the pilot plant level, the primary components of the make-gas (or product gas) are of prime interest — as is the maximization of methane production and the study of the relationship between CO, CO_2, and H_2. The other components, with the exception of H_2S and NH_3, make up a minor fraction of the gasifier product and have to date been largely ignored. Thus, because of this dearth of data, one must treat process gas in any part of the reactor system as if it had the same composition as the off-gas from the reactor itself.

Oils and Tars in the Gas--

In addition to the major quantities of H_2, CO, CO_2, CH_4, and C_2H_6 made in the Synthane gasifier, there are numerous minor constituents. Table 8 shows some of these minor constituents of interest including sulfur compounds and BTX (benzene, toluene, xylene) components. In practice, the BTX components should be removed in the oil scrubber, and the sulfur compounds should be

Table 8. Mass spectrometric analyses of Synthane benzene soluble tar.[a]

Structural Type	Parent Compound		Illinois #6 Coal		Lignite		Montana Sub-bituminous Coal		Pittsburgh Seam Coal	
	Formula	B.P.°C	Vol % Benzene Soluble	ECI Estimate Vol % Gas[b]	Vol % Benzene Soluble	ECI Estimate Vol % Gas[b]	Vol % Benzene Soluble	ECI Estimate Vol % Gas[b]	Vol % Benzene Soluble	ECI Estimate Vol % Gas[b]
Benzenes	C_6H_6	80.1	2.1	0.017	4.1	0.02	3.9	0.026	1.9	0.016
Indenes	$C_6H_4CH_2CH{:}CH$	182.4	8.6	0.048	1.5	0.005	2.6	0.012	6.1	0.034
Indans	$C_6H_4CH_2CH_2CH_2$	176.5	1.9	0.010	3.5	0.011	4.9	0.021	2.1	0.011
Naphthalenes	$C_{10}H_8$	217.9	11.6	0.058	19.0	0.059	15.3	0.061	16.5	0.083
Fluorenes	$C_6H_4CH_2C_6H_4$	295	9.6	0.037	7.2	0.018	9.7	0.03	10.7	0.041
Acenaphthenes	$C_{10}H_6(CH_2)_2$	277.5	13.5	0.056	12.0	0.030	11.1	0.037	15.8	0.066
3-ring aromatics	$C_6H_4{:}(CH_2)_2{:}C_6H_4$	354.5	13.8	0.05	10.5	0.023	9.0	0.026	14.8	0.053
Phenylnaphthalenes	$C_6H_5C_{10}H_7$	325	9.8	0.031	3.5	0.0066	6.4	0.016	7.6	0.024
4-ring pericondensed	ND[c]	ND	7.2	ND	3.5	ND	4.9	ND	7.6	ND
4-ring catacondensed	ND	ND	4.0	ND	1.4	ND	3.0	ND	4.1	ND
Phenols	C_6H_5OH	182	2.8	0.019	13.7	0.056	5.5	0.03	3.0	0.020
Naphthols	$C_{10}H_7OH$	288	ND	ND	9.7	0.026	9.6	0.034	ND	ND
Indanols	$C_6H_4CH_2CH_2{:}CHOH$	ND	0.9	0.0043	1.7	0.0049	1.5	0.0057	0.7	0.0033
Acenaphthenols	ND	ND	ND	ND	2.5	ND	4.6	ND	2.0	ND
Phenanthrols	$C_{14}H_9OH$	168	2.7	0.0089	ND	ND	0.9	0.0023	ND	ND
Dibenzofurans	$C_6H_4OC_6H_4$	287	6.3	0.024	5.2	0.012	5.6	0.017	4.7	0.018
Dibenzothiophenes	$C_6H_4SC_6H_4$	332.3	3.5	0.012	1.0	0.002	1.5	0.004	2.4	0.0083
Benzonaphthothiophenes	ND	ND	1.7	ND	ND	ND	ND	ND	ND	ND

[a] The analyses given are derived from the Bruceton 25 lb/hr coal feed laboratory scale Synthane gasifier. "These may be representative of those gases which will be obtained from a [pilot plant and a] commercial operation [of the Synthane process]." There will be some differences due to both variation in temperature, steam-oxygen feed quantities, and coal. Adapted from the work of Forney et al. (1974).

[b] ECI estimate of concentration in gas phase.

[c] No data.

removed by gas scrubbing (Synthane employs a Benfield hot carbonate gas purification system and activated carbon traps) (Forney et al. 1974). Table 9 shows combined data from two gas chromatographic analyses of the bench scale product. One scan was of soluble oils dissolved in the condensed liquor from the Synthane bench scale unit. The second analysis was of the benzene soluble oils collected in the Synthane bench scale tar trap. The data were obtained at Oak Ridge National Laboratory in conjunction with a project involving oils from a number of sources of synthetic fuels (see also Tables A-1, A-2, and A-3 in Appendix A).

The benzene soluble oils represent approximately 85% of the total oils collected. This is a relatively consistent finding, whether the coal used in the Synthane process is lignite, sub-bituminous, or bituminous. However, tar yields do increase with increasing rank of coal, varying from approximately 3 wt % for lignite to approximately 5 wt % for bituminous coals (Lebowitz et al. 1975). This information was utilized to determine the concentrations of the individually identified components in the reactor product gas, assuming a gas yield of 25 scf/lb coal (Table 10).

Special Cases--
Each plant is a special case. For example, it can be anticipated that the tar yield from the MERC fixed-bed unit may be higher than that from any of the fluid-bed units and that these tars may have a wider boiling range than any others.

Material balances indicate that the HYGAS process produces about the same quantity of liquid hydrocarbons as the free-fall Synthane process already described. However, 95 wt % of the total HYGAS oil in the gasifier off-gas can be defined as follows: 85 wt % toluene, 8 wt % benzene, 3 wt % (and higher) C_9 (Lee 1975) — excluding pretreater tars. The high proportion of light oils is explained as being due to the extraordinarily rapid heat-up in the second entrained flow gasifier, after volatilization of the more reactive components in the first gasifier bed.

The CO_2 Acceptor process emits few, if any, light oils or tars. Undoubtedly any that are produced are absorbed into the circulating dolomite and are coked in the regenerator and thus are destroyed before they can leave the reactor-regenerator system.

The Bi-Gas process is supposed to produce no oils, nor is it likely that the Agglomerating Burner will produce oils. Therefore, the pilot plant designs do not provide for oil production in either process.

Effects of Gasifier Coal Feed Geometry--
Coal may be fed to the gasifier at the top of the bed (fixed-bed reactors, fluidized-bed reactors), at the bottom of the bed, or between these two extremities (fluid beds only). Apparently, the point of coal-feed delivery does not affect the Btu value of the gasifier off-gas, but seems to affect some constituents of the gas. In general, the available data from observations of the difference between CO_2 Acceptor bench scale product composition and pilot plant product composition (oral communication, October 27, 1975, by D. McCoy, CO_2 Acceptor Pilot Plant, Rapid City, South Dakota) and from

Table 9. Organic compounds condensed from the Synthane gasification process (bench scale unit).[a]

Chromatographic Identification	Formula	B.P.°C	Concentration µg/g (ppm)
Acetic Acid	CH_3COOH	118.1	591
Propanoic Acid	CH_3CH_2COOH	141.1	60.5
n-Butanoic Acid	$CH_3CH_2CH_2COOH$	163.5	20.86
Acetamide	CH_3CONH_2	222	ND[c]
n-Pentanoic Acid	$CH_3(CH_2)_3COOH$	187	10.62
Propionamide	$CH_3CH_2CO(NH_2)$	213	ND
n-Hexanoic Acid	$CH_3(CH_2)_4COOH$	205	21.16
Butyramide	ND	ND	ND
Phenol	C_6H_5OH	182	1958.9
n-Heptanoic Acid	ND	ND	ND
o-Cresol	$CH_3C_6H_4OH$	191.5	640.2
m&p-Cresols	$\left\{\begin{matrix}CH_3C_6H_4OH\\CH_3C_6H_4OH\end{matrix}\right\}$	$\left\{\begin{matrix}202.8\\202.5\end{matrix}\right\}$	1740.1 ND
n-Octanoic Acid	ND	ND	ND
2,6-Dimethylphenol	$(CH_3)_2C_6H_3OH$	212	34.48
o-Ethylphenol	$C_2H_5C_6H_4OH$	207.5	28.92
2,5-Dimethylphenol	$(CH_3)_2C_6H_3OH$	211.5	213.9
3,5-Dimethylphenol	$(CH_3)_2C_6H_3OH$	219.5	237.6
2,3-Dimethylphenol	$(CH_3)_2C_6H_3OH$	218	25.86
n-Nonanoic Acid	ND	ND	ND
3,4-Dimethylphenol	$(CH_3)_2C_6H_3OH$	225	101.73
n-Decanoic Acid	ND	ND	ND
α-Naphthol	$C_{10}H_7OH$	288	8.17
β-Naphthol	$C_{10}H_7OH$	294.85	24.65
Naphthalene	$C_{10}H_8$	217.9	0.139
2-Methylnaphthalene	$C_{10}H_7CH_3$	245	1.263
1-Methylnaphthalene	$C_{10}H_7CH_3$	240-3	0.031
Azalene	ND	ND	ND
Biphenyl	$C_6H_5C_6H_5$	254-5	0.0017
2,6-Dimethylnaphthalene	$C_{10}H_6(CH_3)_2$	ND	0.048
1,3 and 1,6-Dimethylnaphthalene	$C_{10}H_6(CH_3)_2$	ND	0.066
Butylated Hydroxytoluene	ND	ND	ND
1,5 and 2,3-Dimethylnaphthalene	$C_{10}H_6(CH_3)_2$	268	0.024
1,2-Dimethylnaphthalene	$C_{10}H_6(CH_3)_2$	ND	0.010
Acenaphthylene	$C_{10}H_6CHCH$	265-75	ND
Acenaphthene	$C_{10}H_6(CH_2)_2$	277.5	IR[b]
Fluorene	$C_6H_4CH_2C_6H_4$	293-5	0.0175
9,10-Dihydroanthracene	$C_6H_4:(CH_2)_2:C_6H_4$	305	0.0022

[a] Adapted from the work of Massey and Dunlap (1976) and Guerin and Epler (1976).
[b] Incomplete resolution.
[c] No data.

Table 10. Components in synthane gasifier gas (25 lb/hr coal feed bench scale gasifier).[a]

			Illinois # 6 Coal		Wyoming Sub-bituminous Coal		Western Kentucky Coal		North Dakota Lignite		Pittsburgh Seam Coal	
		B.P., °C	ppm	vol %	ppm	vol %	ppm	vol %	ppm	vol %	ppm	vol %
Hydrogen Sulfide	H_2S	-60	9800	0.9800	2480	0.2480	2530	0.2530	1750	0.1750	860	0.0860
Carbonyl Sulfide	COS	-50	150	0.0150	32	0.0032	119	0.0119	65	0.0065	11	0.0011
Thiophene	$<(CH{:}CH)_2>S$	84	31	0.0031	10	0.0010	5	0.0005	13	0.0013	42	0.0042
Methyl Thiophene	C_5H_6S	112-116	10	0.0010	ND[b]	ND	ND	ND	ND	ND	7	0.0007
Dimethyl Thiophene	C_6H_8S	137-141	10	0.0010	ND	ND	ND	ND	11	0.0011	6	0.0006
Benzene	C_6H_6	80	340	0.0340	434	0.0434	100	0.0100	1727	0.1727	1050	0.1050
Toluene	$C_6H_5CH_3$	111	94	0.0094	59	0.0059	22	0.0022	167	0.0167	185	0.0185
C_9 Aromatics	ND	ND	24	0.0024	27	0.0027	4	0.0004	73	0.0073	27	0.0027
Sulfur Dioxide	SO_2	-10	10	0.0010	6	0.0006	2	0.0002	10	0.0010	10	0.0010
Carbon Disulfide	CS_2	46	10	0.0010	ND	ND	ND	ND	ND	ND	ND	ND
Methyl Mercaptan	CH_3SH	6	60	0.0060	0.4	0.00004	33	0.0033	10	0.0010	8	0.0008

[a] Adapted from the work of Forney et al. (1974)

[b] No data.

Synthane bench scale data (Massey et al. 1975) would indicate that less of such components as tar, phenol (Table 11), cyanide, and thiocyanate are produced from deep-bed injection than from free-fall injection of the coal (Table 12).

The data presented by Massey et al. (1975), from the 4-inch-diameter Synthane bench scale unit, indicate that for Synthane-produced tar and heteroatomic compounds

- Changes in coal-feed geometry materially affected the quantity of tar produced.
- All samples analyzed had initial boiling points substantially in excess of 100°C (212°F). This suggests that few low molecular weight hydrocarbons such as benzene, toluene, or xylene were produced.
- Thirty to sixty percent of the hydrocarbons present in the samples boiled above 500°C (932°F). Tars collected late during these runs tended to contain less +500°C material, though this shift did not lead to increased Btu production. It is assumed that the Synthane tars will be more like the late run samples collected from the 25 lb/hr coal-feed unit, which generally ran for less than 5 hours.
- Changes in coal injection geometry had little effect on ammonia or H_2S production rates.

Sulfur Compounds--
It has been reported that approximately 90% of the organic sulfur in coal can be expected to be converted to H_2S during gasification (Williams and Dressel 1973). It has also been estimated that 8% of the total sulfur in the feed coal to the Synthane process will remain in the char (U.S. Bureau of Mines 1972), and in the HYGAS process, 0.5 wt % of the sulfur in the coal was found to remain in the char (Lee 1975). Thus, it is obvious that the total quantity of sulfur gasified will depend upon reactor conditions. The distribution of sulfur compounds will be dependent upon the mode of operation, temperature of operation, and coal feed. The available data would indicate that the gasified sulfur may be distributed as shown in Table 13.

Nitrogen--
Nitrogen balances indicate that 78% of the nitrogen in the coal fed to the Synthane Pilot Plant gasifier is converted to ammonia (U.S. Bureau of Mines 1972). Within the accuracy of bench scale data, ammonia production (from the Synthane process) appears to vary from 15 to 20 lb/ton moisture-ash-free (MAF) coal for lignite and to average about 20 to 22 lb/ton (MAF) for Illinois No. 6 coal (Nakles et al. 1975). At the HYGAS Pilot Plant, measured ammonia production yields were constantly below 50% though actual NH_3 production levels were expected to be 15 to 20 lb/ton of coal or a 55% to 70% yield of the total nitrogen in the coal feed (Massey et al. 1976a). In characterizing the effluents of HYGAS, Massey et al. also indicated that the distribution of nitrogen compounds was as shown in Table 14.

Table 11. Decreased phenol production with increased depth of fresh coal injection.[a]

Procedure	Free-Fall Injections, ppm		Shallow-Bed Injections, ppm		
Run No.	CHPFI-49	CHPFI-55	CHPFI-80	CHPFI-96	CHPFI-97
Compound Present					
Phenol	3,400	2,660	1,300	1,270	1,000
Cresols	2,840	2,610	530	890	930
C_2-Phenols	1,090	780	140	270	330
C_3-Phenols	110	100	20	50	50
Dihydrics	250	540	60	20	20
Benzofuranols	70	100	30	40	50
Indanols Acetophenones }	150	100	40	50	60

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[a] Recovered from aqueous condensates from a range of Illinois #6 coal gasification tests (Massey et al. 1975).

Table 12. Steady-state effluent production rates: free-fall, shallow-bed, and deep-bed injections of North Dakota lignite into the Synthane 25 lb/hr bench scale gasifier.[a]

Pollutant lb/ton MAF Coal	Gasification of North Dakota Lignite		
	Free-Fall Injection	Shallow-Bed Injection	Deep-Bed Injection
Tar	74.1 ± 27	10.1 ± 5	6.3 ± 2.2
Phenol	11.9 ± 1.3	3.5 ± 1.9	0.5 ± 0.6
Chemical Oxygen Demand	77.7 ± 14.4	11.8 ± 5.4	3.6 ± 2.4
Total Organic Carbon	22.0 ± 3.3	4.8 ± 1.3	2.7 ± 0.7
Inorganic Carbon [b]	12.5 ± 2.4	11.0 ± 2.3	11.4 ± 2.4
Cyanide	Negligible	Negligible	Negligible
Thiocyanate	0.045 ± 0.083	≤0.016 ± 0.002[c]	≤0.017 ± 0.004[c]

[a] Adapted from Massey et al. (1975).

[b] The relatively constant inorganic carbon production levels reported for different lignite injection positions are expected and reflect the presence of a saturated amount of CO_2 in basic (pH 9) condensate.

[c] Measurements at or below the limiting sensitivity of the analytical method employed.

Table 13. Sulfur distribution.

	Synthane (bench scale)[a]			
Compounds	Illinois #6 Bituminous vol %	North Dakota Lignite vol %	Pittsburgh Bituminous vol %	Lurgi vol %[b]
H_2S	97.2	94.2	91.1	95
COS	1.5	3.5	1.2	2.4
Thiophenes	0.5	1.3	5.8	0.3
SO_2[c]	0.1	0.5	1.1	ND[d]
CS_2	0.1	ND	ND	0.3
Mercaptans	0.6	0.5	0.8	2.0

[a] From the work of Forney et al. (1974).

[b] From the work of Williams and Dressel (1973).

[c] Present in bench scale unit, but should be eliminated in pilot plants.

[d] No data.

Table 14. HYGAS Pilot Plant liquid effluent characteristics, hydrogasification of Montana lignite, Run 37.[a]

Effluent Component	Effluent Production of Nitrogen Compounds lb/ton Coal, MAF[b]	Wt % of Nitrogen Effluent	Estimated Vol % of Reactor Gas Stream (dry basis)
NH_3	13.1 ± 0.3	83.97	0.47
CN^- (x10^6)	28.7 ± 15.7	0.0002	0.67 (x10^{-6})
SCN^-	2.5 ± 0.2	16.02	0.03

[a] Adapted from Massey et al. (1976a).

[b] Reported data represent only *lower bounds* on actual plant effluent production rates. Not included in any steady-state data are effluents contained in oil stripper water condensate, coal mill venturi scrubber water, and condensate depressurization off-gas. In addition, during steady-state period #1, effluents in product gas cyclone slurry water and the oil/water/solids interface from the product gas quench system were not measured.

Because the gasifier atmosphere is reducing (contains excess hydrogen), no NO_x is expected to be produced during the gasification of coal, whether air or oxygen is used. Further, even though NH_3 converts relatively easily to NO_x when combusted, tests conducted on a low-Btu gasifier combustor combination indicated that "the overall conversion of coal nitrogen to NO_x in a gasification/combustion process was significantly less than that which occurs in the direct burning of pulverized coal. These results indicate that the conversion was reduced by a factor of two." (Lisauskas and Johnson 1976)

Trace Elements--
The degree of volatility of all elements and compounds is dependent both upon the characteristics of the element or compound and upon the chemical and physical characteristics of the atmosphere in which the element or compound is placed. A study of the volatility of the trace elements in a hypothetical coal was made by Ruch and Associates (1974) under the reducing atmospheric conditions of a gasifier (Table 15). This study was expanded by Attari (1973), who examined the volatility of coal-contained trace elements at various points in the HYGAS gasifier. The anticipated trace element concentration that might be expected in the make-gas at various parts of Attari's gasifier system has been calculated as shown in Table 16.

These calculations, based upon Attari's data, indicate that, under the conditions specified in Table 16, the concentration of mercury could reach 0.7 ppm in the pretreater off-gas and 1.2 ppm in the gasifier off-gas (HYGAS type system). If pretreater and gasifier are one continuous unit, then at a gasifier temperature of 1830°F (1000°C), the total concentration of mercury in the bed might be 1.6 ppm (Synthane or Bi-Gas type operation). In the HYGAS operation where the liquid in the slurry feed appears in the reactor off-gas stream, the actual concentration of mercury in the gasifier off-gas stream would be more likely to approach 0.9 ppm than 1.2 ppm.

None of the available data indicate what occurs in the gasifier when an element which is volatilized at a high-temperature portion of the reactor passes into a lower-temperature portion of the reactor. It would be normal for the element to condense on the nearest surface, e.g., coal, metal, refractory, etc., and to concentrate at that point.

Problems

Problems in the gasifier system as described will probably consist primarily of plugged lines, hot spots, insulation problems, and leaks. Leaks involve release into the workplace of toxic substances, including the oils and trace elements, estimated in Tables 10 and 16. To rectify any of the problems listed, the reactor would have to be opened, probably after an emergency shutdown.

Gross condensation in the reactor is unlikely unless the top of the reactor cools. Condensation between the reactor and the quench system is possible, particularly when high-temperature tars are produced (Synthane, MERC). Low-temperature distillates such as those produced in HYGAS should not condense prior to being quenched. (These generalizations on condensation will also be valid for pretreater systems. Some of the distillates produced at

Table 15. Trace elements — estimated volatility.

Component	Hypothetical Coal, ppm[a]	Percent Volatile[b]
Chlorine	1,400	90+
Mercury	0.2	90+
Selenium	2.08	74
Arsenic	14	65
Lead	34.78	63
Cadmium	2.52	62
Antimony	1.26	33
Vanadium	32.7	30
Nickel	21.07	24
Beryllium	1.61	18
Chromium	13.75	nil
Zinc	272.2	eg,10
Boron	102.2	eg,10
Fluorine	60.9	eg,10
Titanium	700	eg,10

[a] Analyses taken from Table 5.

[b] Volatility based mainly on gasification experiments (Attari 1975); chlorine is taken from combustion tests; zinc, boron, fluorine, and titanium are estimated at 10% for illustration in absence of data (Jahnig 1975). Adapted from Ruch et al. (1974).

Table 16. Trace element concentration at various stages of the HYGAS gasification process, calculated on a raw coal basis for Pittsburg #8 coal.[a]

Element	Raw Coal ppm	After PT		After HG		After ETG		Total Loss, %	Estimated Trace Element Concentration in Off-Gas, Vol %		
		430°C (806°F)[b]		650°C (1200°F)[b]		1000°C (1832°F)[b]					
		ppm	Loss, %	ppm	Loss after PT, %	ppm	Loss after HG, %		After PT[c]	Between PT and ETG[d]	Total PT + HG + ETG[e]
Mercury	0.27	0.19	30	0.06	68	0.01	19	96	7.1×10^{-7}	1.2×10^{-6}	1.6×10^{-6}
Selenium	1.7	1.0	41	0.65	35	0.44	12	74	1.6×10^{-5}	9.4×10^{-6}	1.9×10^{-5}
Arsenic	9.6	7.5	22	5.1	32	3.4	18	65	5.0×10^{-5}	7.2×10^{-5}	1.0×10^{-4}
Tellurium	0.11	0.07	36	0.05	29	0.04	9	64	5.6×10^{-7}	3.1×10^{-7}	6.7×10^{-7}
Lead	5.9	4.4	25	3.3	25	2.2	19	63	1.3×10^{-5}	1.4×10^{-5}	2.2×10^{-5}
Cadmium	0.78	0.59	24	0.41	31	0.30	14	62	3.0×10^{-6}	3.4×10^{-6}	5.2×10^{-6}
Antimony	0.15	0.13	13	0.12	8	0.10	13	33	2.9×10^{-7}	3.3×10^{-7}	5.0×10^{-7}
Vanadium	33	36	0	30	9	23	21	30	—	2.6×10^{-4}	2.4×10^{-4}
Nickel	12	11	8	10	9	9.1	8	24	3.0×10^{-5}	4.3×10^{-5}	6.0×10^{-5}
Beryllium	0.92	1.0	0	0.94	0	0.75	18	18	—	3.7×10^{-5}	2.3×10^{-5}
Chromium	15	17	0	16	0	15	0	0	—	—	—

PT = Pretreatment HG = Hydrogasification ETG = Electrothermal Gasification

[a] Adapted from Attari (1973).
[b] Maximum temperature.
[c] Basis: Assume 21.2 scf total gas/lb coal, 0.038 lb make and feed water/lb coal, 0.0082 lb make oil/lb coal (IGT 1973).
[d] Basis: Assume 28.7 scf total gas/lb coal, 0.43 lb make and feed water/lb coal, 0.038 lb make oil/lb coal (IGT 1973).
[e] Basis: Assume 21 scf total gas/lb coal, 0.43 lb make and feed water/lb coal, 0.046 lb make oil/lb coal (IGT 1973).

pretreater reactor temperatures will condense in the reactor or in the reactor off-gas line if either the reactor head temperature or line temperature drops below the reactor temperature by only a few degrees.) If condensation does occur, employees will be exposed to the possibility of skin contact with condensed products on the interior vessel walls when it is opened.

Solids in a fluid-bed reactor will most likely be so highly coked or ashed that they are essentially inert. However, this may not be true in a fixed-bed unit. They may also pose a dust hazard.

Ash Removal and Disposal

As stated previously, the composition of material in a fluid bed is an average of fresh feed plus partially and completely reacted materials at operation conditions. Therefore, material discharged from a median-temperature gasifier (Synthane, HYGAS) will contain more carbon than that from a high-temperature gasifier (Bi-Gas) or combustor (Agglomerating Burner). It may be presumed that at the temperature of the gasification reaction, the char product will be reasonably stable and that, therefore, fresh unquenched char will probably present only a dust hazard. The higher the process temperature, the more stable the solid by-products. The fixed-bed gasifier (MERC) is a different case. Here, the highest temperatures are observed near the bottom of the bed, where the devolatilized coal is in contact with the incoming air or oxygen. Temperatures are relatively high and essentially complete combustion takes place. The discharged ash will be stable.

At the Synthane Pilot Plant, char from the fluid bed will flow into one of two lockhoppers, similar to those of the Petrocarb system already described for the coal-feed system. In the ash system, the bottom of the gasifier is comparable to the weigh-hopper, the ash lockhoppers to the storage injector, and the low-pressure char slurry tank to the primary coal injector, except that, here, the bottom of the gasifier is pressurized while the char slurry tank is at atmospheric pressure.

From the char lockhopper, the char is conveyed pneumatically with low-pressure steam to the low-pressure agitated slurry tank through a cold water venturi nozzle. The venturi insures complete wetting of the char. Water to the venturi is supplied by circulation of the tank contents. Any gases (primarily steam or oxygen) released from the gasifier with the char are vented from the tank to the atmosphere. From the low-pressure agitated slurry tank, the cooled slurry is pumped to the agitated slurry filter feed tank. (In case of emergency, the lockhopper system can be bypassed and the hot char conveyed to a high-pressure slurry tank. Slurry is depressurized through a flow control valve to the slurry filter feed tank, which is, presumably, vented to the atmosphere.) The char slurry is then pumped to one of two continuous filters. The 150°F (65°C) filtrate is cooled and recirculated to the slurry tank in current operation. The filter cake (char containing ∿ 15-25 wt % water) is conveyed to a storage pile, and then to disposal (U.S. Bureau of Mines 1972).

Special Cases--

The HYGAS Pilot Plant char removal system is similar to the Synthane emergency system. The primary difference is that from the high-pressure slurry tank, the slurry is pumped through a de-energizer (spared) for pressure reduction.

Gas dissolved in the slurry is vented to the atmosphere. After depressurization, the char slurry stream joins the several venturi scrubber water streams at the Edens separator (IGT 1973), to be separated and filtered as previously described.

Ash from the CO_2 Acceptor system is sufficiently fine to be elutriated from the regenerator, removed from the gas stream with cyclones, and dropped into a lockhopper-slurry system similar to the one described for the Synthane plant. The slurry is dumped into the wastewater pond for eventual recovery and burial in a clay-lined pit. Other char and limestone purge systems employ lockhoppers and tote bins. Tote bin contents are also buried (Evans 1976a; Stearns-Roger 1976b).

Analyses-

Char analyses are shown in Table 17. The differences in the carbon-to-ash ratios reflect the differences in the process variables.

Analyses of trace elements in the water from Synthane and CO_2 Acceptor are depicted in Table 18. It should be noted, however, that in both cases this water is recycled filtrate. (It is of interest that the values for phenol and several trace elements in the Rapid City municipal water are the same as or higher than those for the process pond water.)

Problem Areas--

Leaks--In the ash system, the primary problem is the probability of leaks in the lockhopper valves and/or the formation of plugs in the system. If these valves do leak, process gas from the vessel may be vented into the atmosphere, depending on the size of the leak and the process flows.

Toxicity--In general, it would appear that the ash or chars themselves are essentially inert. However, because of the large surface areas common to most chars, they may act as oil or tar adsorbers when they are dumped into or slurried with water that contains make-oil/tar, dissolved or suspended. By the same mechanism, they may also concentrate the dissolved trace elements from the recycle water. Then, although the trace elements in the char or ash may be inert (i.e., tied up in the carbonaceous and ash materials within the coal), the adsorbed trace elements would be easily removed by leaching. (Alternatively this possibility for adsorption might be exploited to clean up pond water.)

Radioactivity--There has been some concern expressed about radioactive coal ash as certain coals in the Rocky Mountain Region have been shown to contain uranium. Some of these coal deposits contain 0.005% to 0.01% uranium, and deposits in local areas may contain higher percentages. Investigations by the U.S. Geological Survey suggest that lignites may contain the most uranium, and sub-bituminous B and C coals the next largest concentrations. Uranium-bearing coal is present in Wyoming, Colorado, New Mexico, and southeastern Idaho. The higher ranked bituminous coals and anthracite of the central and eastern United States rarely contain more than 0.001% uranium (Magee et al. 1973).

Table 17. Char and ash analyses.

	HYGAS	CO_2 Acceptor	Synthane	
	Lignite[a]	Lignite[b]	Bituminous[c]	Lignite[d]
Hydrogen	0.76	0.00	1.0	1.2 ± 0.2
Carbon	34.49	7.38	72.4	52.4 ± 4.8
Nitrogen	0.19	0.00	0.5	0.5 ± 0.1
Sulfur	0.17	0.00	0.4	0.3 ± 0.1
Oxygen	3.26	0.00	1.8	3.9 ± 0.8
Ash	61.13	90.79	23.9	41.9 ± 5.3
CaS - CaO	ND[e]	1.83	ND	ND

[a] Adapted from Lee (1975).
[b] Adapted from Fink et al. (1975).
[c] Data from pilot plant drawings (U.S. Bureau of Mines 1972).
[d] Data from 25 lb/hr bench scale reactor (Nakles et al. 1975).
[e] No data.

From measurements of gamma activity, it has been determined that the content of radioactive elements in coal is generally less than that in sedimentary rocks (Magee et al. 1973). Thus, it appears that radioactive ash would rarely be a problem. Should the ash be sufficiently radioactive to present a problem, it should be handled as if it were a uranium ore and should be further processed to recover its nuclear fuel value.

Analytical Difficulties--Massey (Project Manager of the ERDA-sponsored "Gasification Pilot Plant Environmental Assessment Project") has expressed concern about the accuracy and representativeness of either single grab samples or 8-hour samples of condensate or gas streams. He has obtained data which indicate that this type of pilot plant sample can be highly variable. The data may indicate, for example, that component A is disappearing while component B is increasing and the concentration of C is stable. This sequence is especially true when one is looking for very small concentrations of materials. However, unwary extrapolation of such data would lead to incorrect results (Evans 1976a). Such variability in minor element sampling is not only possible, but quite likely at the pilot plant. Of special concern is preservation of the samples, as coal conversion liquid products or water (liquor) samples tend to be highly unstable.

GAS QUENCH AND SCRUBBING SYSTEM

Venturi Water Scrubber

Synthane gasifier off-gas contains solids, tars*, and oils*, which must be removed prior to downstream use. It must also be cooled. The quench system in most general use is the water venturi scrubber followed by a scrubber surge tank and secondary scrubbing (Figure 8).

In the Synthane plant, the 1400°F (760°C) reactor off-gas is contacted with 350°F (177°C) recycle water. The venturi action atomizes the scrubbing water, which provides a high contact surface and cools the gas to 445°F (229°C). This is the best available means for intimate water/gas contact and for water scrubbing. The cooling effect condenses both excess water and some tars. The gas-water mixture flows into a scrubber surge tank, where the gas separates and passes into the raw gas scrubber. The water, now containing tar, dissolved gas, and solids, is fed through a centrifugal pump (spared). From the pump, the venturi feed water flows through a cooler (spared), which cools the

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*It is estimated that the Synthane gasifier off-gas will contain 212 lb per hour of oils and tars, assumed to be divided in the following manner (see Appendix E):

	Light Oil	Middle Oil	Heavy Oil	Residue
Estimated molecular weight	150	190	230	400
Estimated average boiling point, °C	168.5	260	413	510
Estimated weight, lb/hr	10.6	61.5	55.1	84.8

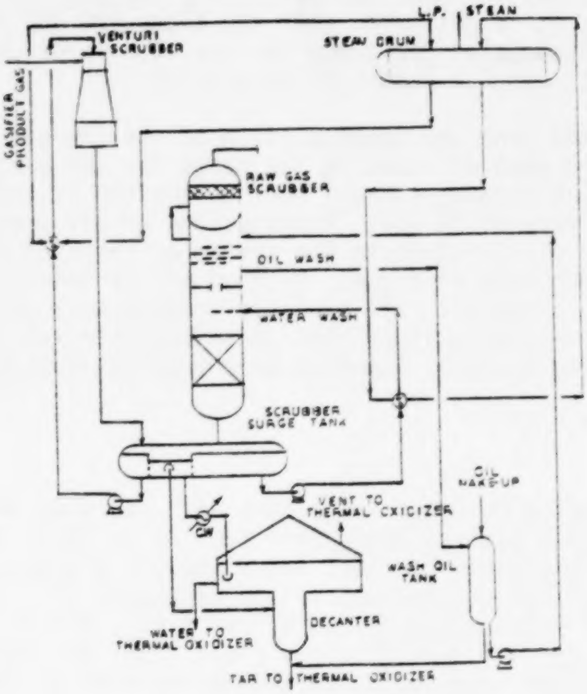
L.P. STEAM
VENTURI SCRUBBER
STEAM DRUM
GASIFIER PRODUCT GAS
RAW GAS SCRUBBER
OIL WASH
WATER WASH
SCRUBBER SURGE TANK
OIL MAKEUP
VENT TO THERMAL OXIDIZER
CW
WASH OIL TANK
DECANTER
WATER TO THERMAL OXIDIZER
TAR TO THERMAL OXIDIZER

Figure 6. Gas quench and scrubbing system — Synthane Pilot Plant.

venturi feed water while producing low-pressure steam from boiler feed water. No regular makeup water is supplied, as off-gas condensate should supply all that the system requires.

Raw Gas Scrubber

In a second system on the scrubber surge tank, water is taken from the surge tank to a second centrifugal pump (spared), through a second cooler (spared), to the top of the lower section of the raw gas scrubber. Here the gas is recontacted with the scrubbing water, first in a baffled section, and then in a packed bed for further removal of elutriated solids or tar. The water is then returned to the scrubber surge tank. If required in the Synthane process, an oil scrubber is available.

If the oil scrubber is used, the gas passes through a series of oil-laden baffle plates, and then through a demister placed at the top of the vessel. Emerging gas temperature will be 330°F (165°C). The gas stream should then be free of heavy tar, solids, and excess water. Some gas and light hydrocarbons will be dissolved in both the scrubber water and the wash oil. Alternatively, vapor pressure calculations indicate that light oils formed will be coal-derived distillate, probably boiling in the 400° to 600°F (204° to 316°C) range, may be vaporized out of the raw gas scrubber. (Based on these calculations, it is estimated that the clean raw gas from the scrubbers in the Synthane Pilot Plant may contain 10.6 lb/hr of light oil, 82 lb/hr of middle oil, and 0.1 lb/hr of heavy oil.)

The wash oil is recycled from the upper portion of the raw gas scrubber to the wash oil tank. The wash oil tank is the surge for the centrifugal wash oil pump (spared), which returns the oil back to the top of the raw gas scrubber at a maximum rate of 24 gpm. (Each gallon of oil scrubs ∿ 107 scf of gas per hour.) Makeup oil is added to the system as required by a reciprocating pump at a maximum rate of 5 gpm. Drained oil is sent to the decanter via an oil drain tank. This oil will probably contain most of the heavy oil and some residue. It is also obvious that these concentrates of higher boiling components will progressively increase as the gas strips out the lighter components.

Decanter

Excess condensate from the scrubber surge tank will overflow into the decanter. It will be cooled (cooler spared) from 396°F (202°C) to 180°F (82°C), then depressurized through a pressure control valve (double blocked and bypassed) from 1000 psig to atmospheric pressure. It is estimated (U.S. Bureau of Mines 1972) that this water will contain 0.9 wt % CO_2, 0.8 wt % NH_3, up to 3.9 wt % tar and oil, and 0-9.9 wt % solids (coal fines and char). Decanted water goes to a wastewater receiver to be either recycled to the gasifier or pumped (pump spared) to the thermal oxidizer. Gases dissolved in the scrubbing water at high pressure are released to the thermal oxidizer. Decanted tar and solids may be either recycled back to the gasifier for gasification (reciprocating pump spared) or disposed of by thermal oxidation.

Problems

There are a number of potential problems in the gas quenching and scrubbing systems, many of which depend specifically on the product and product mix being handled.

If the gasifier product contains heavy tar, this tar may condense in some of the cooler inlet portions of the venturi piping, as previously described. If condensation does occur, solids will collect in the tar while the tar is simultaneously undergoing polymerization. Next, the shearing action plus the rapid quenching in the venturi may form tar fog (submicron aerosol of condensed tar particles). Such a fog is difficult to precipitate, except by thorough oil scrubbing. If sufficient heavy tar is present in the venturi discharge liquid, an extremely stable emulsion will be formed in the scrubber surge tank. (Coal or char fines will add to the emulsion stability.) Another potential problem in the scrubber surge tank is the buildup of sludge (solids and tars) in the bottom of the tank, with subsequent possible plugging of the venturi scrubber recycle pump suction line.

The venturi scrubber recycle pump will have to pump solids, which could cause excessive wear. This pump also circulates some coal-derived oils, which could affect pump seals, i.e., unless a proper choice of seal is made. It is also possible that solids will collect in the raw gas scrubber section of the scrubber surge tank and cause similar problems in this pump. The two recycle water coolers may also be subject to heavy wear due to solids in the recycle water. Further, it is possible that tar deposition will occur at the cold ends of these coolers. Such deposition is a function of tar molecular weight and the temperature differential between the coolant and the fluid being cooled.

In the lower (water) portion of the raw gas scrubber, sludge may accumulate either on any of the plates or in the packed bed. Likewise, sludge could accumulate on the oil-side plates or in the demister screen. Such accumulation will decrease the efficiency of oil-gas contact and increase the pressure differential across the unit.

The scrubber surge tank overflow water cooler will be subject to wear or tar deposition, and the letdown valve downstream from the cooler will be subject to rapid wear from both dissolved gas release and solids.

The list of possible problems described for the scrubber system and scrubber surge tank is multiplied in the decanter and the decanter oil and water transfer pumps. While the higher temperatures in the surge tank may reduce emulsion formation, letdown of the cooled condensate across the letdown valve will promote their formation. Sludges will also form in the bottom of the decanter and in the decanter oil well.

The problems described for the scrubber and decanter systems will cause operating difficulties, which will necessitate frequent visual inspection, cleaning, and maintenance of equipment. Vessel cleaning will often require entry by the cleaning crew, especially for the removal of sludges. It will also be necessary to see that the sludges are correctly handled during cleaning to reduce spills, and that the sludge is disposed of properly. Available data do not indicate that planned procedures for this operation are widely disseminated.

Special Cases

The venturi scrubber-quench section just described is similar to those in many of the major plants, as the requirement for removal of solids is universal. However, the HYGAS plant uses a system of sequential quench towers instead of a venturi scrubber for scrubbing and quenching the reactor off-gas. The remainder of the HYGAS system is also unconventional. Use of toluene as the feed slurry liquid in the HYGAS plant means that the magnitude of any tars generated in the reactor may be overwhelmed by the presence of the toluene.* It has been necessary to install a two-stage quench and a light oil stripping section in the HYGAS Pilot Plant to insure recovery of make- and slurry-oil (Institute of Gas Technology 1975). Therefore, tar or tar deposits from the gasifier will probably present few problems. At the HYGAS plant, solids from all of the venturi or quench systems go to an Edens separator for recovery.

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*Data indicate that the HYGAS oil is 85 wt % toluene, 8 wt % benzene, and 3 wt % C_9 hydrocarbons (Lee 1975). Discussion at the HYGAS plant indicated that the top end point for this oil is normally 550°F (228°C) with an occasional 650°F (343°C) observed.

(This unit is essentially a settling and drag tank. Coarse settled solids are removed with a chain conveyor to a pile for subsequent disposal.) Fines from the separator are removed via a precoated filter, and "clean" water is returned to the wastewater pond. At the pilot plant, the Edens separator, the filter, and the wastewater pond are open to the atmosphere. The water in each of these unit operations does contain dissolved light oil. When hot water is pumped into the wastewater pond, it may tend to steam distill some light oils into the atmosphere.

Water from the venturi scrubbers at the CO_2 Acceptor Pilot Plant goes directly to the wastewater pond. Solids are filtered out of the water with hay filters and the water is recirculated. A system was installed for oil recovery but no oils or only trace quantities of oil were generated; the oil recovery system therefore is no longer used (Massey et al. 1976b; Evans 1976a).

The Agglomerating Burner is not expected to produce tars or oils. If any are produced, they will be skimmed from the venturi scrubber recycle water and fed directly to the thermal oxidizer with the product gas and burner off-gas.

Product gas and recovered oils from the MERC unit are fed directly to a thermal oxidizer.

No product oils are anticipated from the Bi-Gas plant. Venturi scrubber solids are settled in a wastewater pond for eventual recovery and disposal.

Composition of Coal Gasification Condensates

The condensate or quench water, in addition to having gross quantities of oil, tar, and solids mixed into it, also contains dissolved measurable quantities of heterocyclic and hydrocarbon compounds. Further, if the volatilized trace metals are to be removed from the gasifier product gas, they must be removed either in the scrubbing water, in the scrubbing oil, or in a guard bed. Available data would indicate that appreciable quantities of these trace metals are found in the condensate or gas scrubbing liquors (Table 18).

The gross quantities of solids, tars, or oils can be separated from the water by decanting or settling.* After these treatments, the water will still contain finely divided solids and dissolved materials, as illustrated in Tables 18 and 19. (This Synthane benchscale information should not be accepted as the final word for that process, but it is indicative of relative values of the components that may be found in the effluent.)

Prior to disposal, recovered tars and oils are stored in tank yards within the plant area. Vent gas compositions for two HYGAS systems are given in Table 20. These should be considered as indicative of values only at the

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* It should be noted that since these solids have been in the scrubbing system, they may have adsorbed a relatively large quantity of oil or trace metals, which could be readily leached. If the solid material or the water is incinerated, these trace elements will be released into the atmosphtere — a matter of little concern at the pilot plant level because of both the dilution factor and the relatively small quantities of coal being converted.

Table 18. Trace elements in condensate, coal gasification tests.[a]

Trace Elements in Condensate	Synthane[b] Run #1	Synthane[b] Run #2	CO_2 Acceptor[c]
	Bituminous	Coal	Lignite
	Parts per Million		
Calcium	4.4	3.6	*
Iron	2.6	2.9	*
Magnesium	1.5	1.8	171
Aluminum	0.8	0.7	ND[d]
Chlorine	ND	ND	7
Sodium	ND	ND	80
	Parts per Billion		
Selenium	401	323	ND
Potassium	117	204	86,000
Barium	109	155	ND
Phosphorus	82	92	ND
Zinc	44	83	ND
Manganese	36	38	40
Germanium	32	61	ND
Arsenic	44	28	ND
Nickel	23	34	ND
Strontium	33	24	ND
Tin	25	26	ND
Copper	16	20	ND
Columbium	7	5	ND
Chromium	4	8	ND
Vanadium	4	2	ND
Cobalt	1	2	ND

*Less in pond water than in city water.

[a] For a commercial coal-to-gas plant, this water would be purified as completely as possible and then used as recycled cooling water. Adapted from Massey et al. (1975).

[b] Analyses of the Synthane 25 lb/hr bench scale gasifier condensate performed by the EPA at its Southeast Environmental Research Laboratory for trace elements in the water. Adapted from Forney et al. (1974).

[c] Process pond water values less city water values.

[d] No data.

Table 19. Composition of effluent condensate.

	HYGAS Pilot Plant Montana Lignite[a]									Synthane 25 lb/hr Bench Scale Gasifier						CO_2 Acceptor North Dakota Lignite Process Water Holding Pond[f]	
	Product Gas Quench Condensate		Oil Stripper Bottoms		Gasifier Ash Slurry Water		Discharge from Holding Pond		Effluent Production lb/ton Coal, MAF[b]	Illinois No. 6 Bituminous[c]	Pittsburgh Seam Bituminous[c]	Western Kentucky Bituminous[c]	Wyoming Sub-bituminous[c]	North Dakota Lignite[c]	North Dakota Lignite[d] lb/ton MAF Coal[e]		
	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.								Min.	Max.
pH	7.7	8.3	9.2	9.9	7.0	10.2	8.8	10.6	--	8.6	9.3	8.9	8.7	9.2	--	7.8	8.9
Phenols, mg/l	1,480	2,680	185	1,560	0.008	0.745	212	612	11.4 ± 2.4	2,600	1,700	3,700	6,000	6,600	11.9 ± 1.3	0.001	0.017[l]
NH_3, as N, mg/l	2,980	5,000	10	251	3.12	4.75	54	540	13.1 ± 0.3	8,100[i]	11,000	10,000	9,520	7,200	--	242	296
TOC, mg/l	3,876	4,948	3,192	13,560	25	384	505	10,704	89.1 ± 15.4	--	--	--	--	--	22.0 ± 3.3	--	--
$S^=$, mg/l	120	138	0.03	0.03	<0.003	<0.01	<0.01	108	8.2 ± 0.1	400[j]	--	--	--	--	--	0.01	0.48[m]
CN^-, mg/l	<0.001	<0.001	0.001	0.007	<0.001	<0.001	670	1,920	$(28.7 \pm 15.7) \times 10^{-6}$	0.6	0.6	0.5	0.23	0.1	Negligible	0.02	0.92
SCN^-, mg/l	270	780	128	420	0.2	5	0.001	0.007	2.5 ± 0.2	152	188	200	23	22	0.045 ± 0.003	--	--
TDS, mg/l	1,352	2,168	684	6,154	370	20,078	2	134	12.4 ± 0.6[g]	--	--	--	--	--	--	1,002	2,988
TSS, mg/l	20	52	28,530	59,076	225	96,052	908	27,292	--[h]	600	23	55	140	64	--	257	2,988
Toluene, wt %	0.004	0.007	--	--	--	--	0.001	(?)	--	--	--	--	--	--	--	--	--
Hexane-soluble oil, mg/l	--	6,328	6,328	8,567	8	11	35	95	--	--	--	--	--	--	--	--	--
COD, mg/l	--	--	--	--	--	--	--	--	--	15,000	19,000	19,000	43,000	3,800	77.7 ± 144	15	36
Chloride, mg/l	--	--	--	--	--	--	--	--	--	500	--	--	--	--	--	--	--
Carbonate	--	--	--	--	--	--	--	--	--	6,000[k]	--	--	--	--	--	--	--
Bicarbonate	--	--	--	--	--	--	--	--	--	11,000[k]	--	--	--	--	--	--	--

TOC = Total organic carbon TDS = Total dissolved solids TSS = Total suspended solids COD = Chemical oxygen demand

[a] Adapted from the work of Massey et al. (1976a).

[b] Reported data represent only lower bounds on actual plant effluent production rates. Not included in any steady state data are effluents contained in oil stripper water condensate, coal mill Venturi scrubber water, and condensate depressurization off-gas. In addition, during steady-state period #1, effluents in product gas cyclone slurry water and the oil/water/solids interface from the product gas quench system were not measured.

[c] Adapted from the work of Forney et al. (1974).

[d] Adapted from the work of Nakles et al. (1975).

[e] Tar lb/ton MAF coal = 74.1 ± 27.

[f] Adapted from the work of Massey et al. (1976b).

[g] TDS data from steady-state period #4 are not included in the reported average. A review of the TDS data for all samples of gasifier ash slurry water during Run 37 indicates that the value reported for the single test in steady-state period #4 is in error.

[h] Data gathered were not believed to be sufficiently representative to form a basis for proper characterization of TSS.

[i] 85 percent free NH_3.

[j] $S^= = 400$; $SO_3^= = 300$; $SO_4^= = 1,400$; $S_2O_3^= = 1,000$.

[k] Not from same analysis.

[l] City water = 0.004

[m] $S^= = 0.48$; $SO_3^= = 4.12$; $SO_4^= = 300$.

Table 20. HYGAS Pilot Plant, vent gas compositions, Montana lignite.[a]

Component[b]	Gas Composition, vol %			
	Oil Stripper Vent Gas[c] Run 37		Light Oil Storage Tank Run 37	
	Minimum	Maximum	Minimum	Maximum
N_2	19.6	22.5	4.3	27.
CO	CND[d]	0.8	ND[e]	1.5
CO_2	56.8	61.0	50.2	7.5
H_2	8.3	10.9	6.7	9.0
H_2S	0.1	0.7	ND	0.
CH_4	5.6	9.8	9.0	12.3
C_2H_6	0.5	1.1	1.0	1.7
C_3H_8	ND	0.2	0.01	0.4
C_4H_{10}	0.2	0.3	0.2	0.4
C_5H_{12}	ND	0.07	ND	0.1
C_2H_4	ND	ND	ND	0.1
C_3H_6	ND	0.1	0.06	0.2
C_4H_8	ND	0.2	ND	0.4
C_5H_{10}	ND	0.06	0.07	0.2
C_4H_6	ND	0.03	ND	0.03
C_5H_8	ND	0.01	ND	0.02
C_8H_{10}	ND	ND	ND	0.01
C_2H_2	ND	0.01	ND	0.03
Ar	ND	0.02	ND	0.02

[a] Adapted from the work of Massey et al. (1976a).

[b] Components not analyzed include NH_3 and HCN.

[c] Vent gas flow rate, 81 to 165 lb/hr.

[d] Component not detected.

[e] No data.

time and place they were taken. "What little information is available on gaseous effluents (from the second generation pilot plants), in particular sulfur (and nitrogen), is based strictly on thermodynamic arguments; and no comprehensive gas or solid effluent data have been taken, as yet, which could serve as a reference for evaluation of published data (or of the process itself)" (Massey et al. 1976a).

Hot Gas Cleanup

Hot gas cleanup of low-Btu gas has not yet been considered here. These processes attempt to retain the sensible heat of the low-Btu gas — which represents a considerable fraction of the total available heat from such gases while at the same time removing from the gas the objectionable contaminants, i.e., solids, trace metals, H_2S, and the other sulfur- or nitrogen-bearing compounds. Two benchscale units are being tested at MERC. One process under test utilizes an iron oxide fly ash adsorbent which has removed 97% to 98% of the sulfur (H_2S) in hot (1300° to 1500°F [704° - 816°C]), low-Btu gas, and shows an adsorption capacity of 10-12 wt %. An iron-oxide silica adsorbent that permits operation at temperatures of up to 1700°F (927°C) has also been developed (Lewis et al. 1974; Seamans and White 1976). A two-part paper study on high-temperature particulate removal and sulfur capture is being sponsored by the Electric Power Research Institute. To date, no new developments from this study have been published (Andrews 1976). In any case, these systems are in very early stages of development.

Medium-Btu Gas

At this point in the gasification process, a relatively clean medium-Btu gas has been produced. All particles and heavy tars have been removed from the gas (at the Bi-Gas plant a pair of alumina filters have been placed upstream of the shift conversion unit to insure solids removal), and the water, light oil, and medium oil contents have been reduced. In the low-Btu processes, the gas is ready for "drying" or for use; no further processing of the gas is necessary. In pipeline gas manufacturing plants, the medium-Btu gas is ready for further processing.

SHIFT CONVERSION

The water-gas shift reaction

$$CO + H_2O \longrightarrow CO_2 + H_2$$

is performed to adjust the hydrogen:carbon monoxide ratio in the raw gas to 3:1, the required ratio for carrying out the methanation step.

In the Synthane process (see Figure 9), the clean gas from the raw gas scrubber is divided, half of the gas bypassing the shift converter system and half passing through it. The gas to the converter is heated and steam is added, and the mixture is then passed down through a packed catalyst bed. The usual catalyst for this reaction is cobalt-molybdenum on an alumina base. (This catalyst is being tested so that its capacity for thiophene destruction can be observed.) The exothermic reaction raises the inlet gas temperature from

720°F (382°C) to 825°F (441°C). The shifted gas then rejoins the main gas stream and the entire stream is cooled to 125°F (52°C) as the acid-water condensate is drained to the decanter. It is estimated that the heavy oil has essentially been eliminated at this point, that the middle oil has been reduced to 0.16 lb/hr, and that the light oil is unaffected.

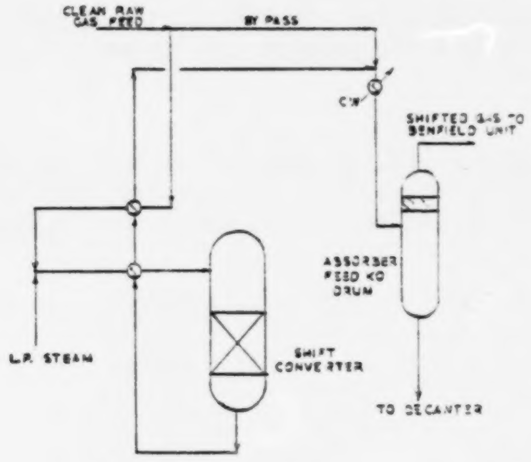

Figure 9. Carbon monoxide shift conversion — Synthane Pilot Plant.

Problems

No outstanding problems are foreseen for the shift conversion operation. It is possible that wash oil could be cracked on the shift catalyst, resulting in carbon deposition, or that a large gasifier surge could deposit solids on the shift converter bed, plugging it. It is also possible that some catalyst breakage may occur, which could result in catalyst dust's being carried downstream. However, in normal operation or for normal maintenance functions, no extraordinary hazards are foreseen other than the presence of high concentrations of carbon monoxide in the vessels.

Special Cases--
Neither HYGAS nor CO_2 Acceptor employs a shift converter. In the case of the CO_2 Acceptor the H_2:CO ratio is approximately 3:1. (The HYGAS product has a H_2:CO ratio of 2 to 4.5:1. The commercial HYGAS plant will need to employ a CO shift unit.)

GAS PURIFICATION

General Discussion

Before the raw gas is upgraded to pipeline specifications by methanation, all sulfur compounds must be removed from the methanator feed gas. If they are not removed, the methanation catalyst will be "poisoned" and its activity severely reduced. Further, carbon dioxide must be separated from the combustible product to achieve the pipeline heating value of 1000 Btu per scf.

A variety of processes is available for simultaneously separating carbon dioxide and hydrogen sulfide from the product gas stream.

Process Discussion

The Benfield process is used for acid gas removal at both the CO_2 Acceptor and Synthane pilot plants (see Figure 10). This process uses a hot carbonate solution with diethanolamine as the activating agent, and is based on the following overall reactions:

$$K_2CO_3 + CO_2 + H_2O \longrightarrow 2\ KHCO_3$$

$$K_2CO_3 + H_2S \longrightarrow KHS + KHCO_3$$

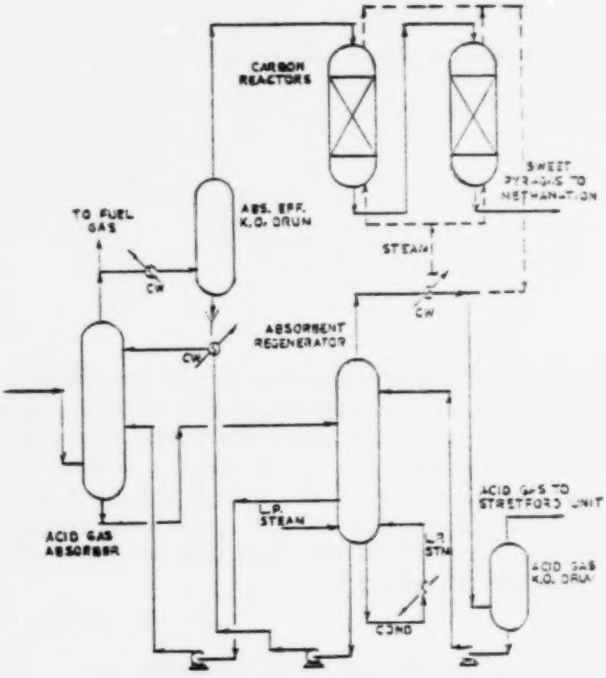
CARBON REACTORS
SWEET PYR-GAS TO METHANATION
TO FUEL GAS
ABS. EFF. K.O. DRUM
CW
STEAM
CW
ABSORBENT REGENERATOR
CW
ACID GAS TO STRETFORD UNIT
L.P. STEAM
L.P. STM
ACID GAS ABSORBER
ACID GAS K.O. DRUM
COND

Figure 10. Acid gas scrubbing — Benfield system, Synthane Pilot Plant.

The hot potassium carbonate process adsorbs H_2S readily, and reduces it to trace quantities in the sweet gas. Carbon dioxide is adsorbed less readily and its concentration is higher (approximately 4%) in the sweet gas.

An added advantage of the carbonate process is that both carbon disulfide and carbonyl sulfide can be removed from the gas stream without significant degradation of the solution. Carbonyl sulfide, for example, will hydrolyze as follows:

$$COS + H_2O \rightleftharpoons CO_2 + H_2S$$

The products of the hydrolysis will then react as shown in the equations already presented.

At the Synthane Pilot Plant, the cold (125°F [52°C]), sour process gas enters the bottom of the absorber and passes upward in countercurrent contact with the descending lean 226°F (108°C) potassium carbonate solution. In the top tray, 125°F (52°C) potassium carbonate is introduced to lower the total acid gas concentration. The sweetened gas leaves the top of the absorber at 130°F (55°C) (see Table 21). Because of the difference in gas-carbonate temperatures, no hydrocarbons will condense in the absorber.

In the Synthane Pilot Plant, approximately 70% of the sweetened gas is used as fuel for plant furnaces or burned in the thermal oxidizer. The remaining 30% of the gas containing 3.26 lb/hr light oil and 0.072 lb/hr middle oil is cooled to 95°F (35°C) for removal of excess water. Upon cooling, the middle oil content of the gas drops to less than 0.01 lb/hr and the light oil content drops to 0.8 lb/hr due to condensation.

Rich carbonate solution leaves the bottom of the absorber and flows to the stripper, which operates at about 50 psig. The sudden release in pressure flashes a large portion of the acid gases at the top tray of the stripper. The partially stripped solution then flows downward through the stripper for further regeneration by stripping steam from the reboiler.

The acid gases, together with some water vapor, pass overhead from the stripper and through a condenser. The steam is condensed and separated from the acid gases in the reflux accumulator. From the reflux accumulator, water is returned to the stripper as reflux and acid gases flow to the thermal oxidizer or go to a Stretford unit for further processing.

Regenerated solution from the bottom of the stripper is pumped to the top of the absorber for reuse. The temperature at the bottom of the stripper will normally run about 237°F (114°C) (Maddox 1974).

Problems--

No unusual problems are foreseen in the gas purification section (see the section on nitrosamines below). As the potassium carbonate is an electrolyte, stress corrosion may occur; however, potassium disulfide formed from the H_2S reactions should act as a corrosion inhibitor. Trace impurities in the gas may form undesirable side reactions, but these can be minimized by removing

Table 21. Gas purification: Synthane Pilot Plant.[a]

Component	Sour Gas mol/hr	Sweet Gas mol/hr
Hydrogen	107.0	106.2
Carbon Monoxide	34.7	34.6
Carbon Dioxide	145.7	2.3
Methane	84.1	83.6
Ethane	2.7	2.7
Nitrogen	6.1	6.1
Hydrogen Sulfide	2.6	<10 ppm
Water	0.8	0.6
Pressure, psig	965	964
Temperature, °F	125	130
°C	51.7	54.4

[a] Adapted from U.S. Bureau of Mines (1972).

a small sidestream (purge) from the unit. Erosion problems may also occur, especially at the lean solution pump and at the pressure reduction valve. These problems could lead to leaks in the system unless maintenance checks on the equipment are made regularly.

It should be noted that the acid gas from the gas sweetening process now contains much higher concentrations of H_2S, COS, CS_2, CH_3SH, and thiophenes than was heretofore possible. Leaking gases and vapors in this portion of the system (to and including the sulfur recovery section) would be exceedingly toxic.

Special Cases--

The HYGAS Pilot Plant uses the diglycolamine process for gas purification. In this process, H_2S is removed to pipeline specifications while CO_2 is completely removed. The diglycolamine will react with both carbonyl sulfide and carbon disulfide (see Table 22). These reactions are irreversible in the normal regeneration cycle. The sweet gas leaving the absorber at 100°F (38°C) will contain some toluene, but no problems seem to have developed at the HYGAS plant. There may be one problem encountered in the diglycolamine absorber not seen with the Benfield unit — foaming. According to Maddox (1974), foaming can be caused by the following:

- Suspended solids
- Condensed hydrocarbons
- Almost any other foreign material

The use of diglycolamine or other amine absorbers poses the potential problem of nitrosamine formation if the amine comes in contact with NO_x compounds (Neurath 1972). While it is doubtful that NO_x compounds would be generated in the gasification process (Lisauskas and Johnson 1976), it is possible that the amine could leak to the atmosphere. In the open air it is much more possible for the amine to come in contact with the NO_x compounds in the atmosphere — for example, from nearby electrical generating stations, plant thermal oxidizers, steam generators, or normal air pollution.

At the Bi-Gas Pilot Plant, the Selexol process has been chosen for gas purification. The Selexol solvent is the dimethyl ether of polyethylene glycol (DMPEG).

The basic Selexol process flow scheme (Figure 11) is simple. Dehydrated sour gas is contacted with the DMPEG solvent at high pressures to adsorb the acid gas constituents. The acid gas solubilities in DMPEG are essentially proportional to the partial pressures of the acid gases. Hydrogen sulfide is significantly more soluble than CO_2 in DMPEG. Therefore, some selectivity for H_2S can be designed into the absorption system. The heat of absorption with the DMPEG solvent and the acid gas system is negligible so that the increase in solvent temperature across the absorber is insignificant (Maddox 1974).

The DMPEG shows a preferential selectivity for acid gases as opposed to hydrocarbons. Methane may be included among those hydrocarbons absorbed though the higher molecular weight hydrocarbons are more soluble than the lighter hydrocarbons. Intermediate distillation of these absorbed hydrocarbons by flash depressurization is required to remove them.

Table 22. Sulfur components in acid gas stream, Run 37, HYGAS Pilot Plant Montana lignite. [a]

Compound	Chemical Formula	Scrubbed Gas from DGA Scrubber (ppm)	Purified Gas After Guard System (ppm)
Methyl mercaptan	CH_3SH	0.0050	0.0032
Methyl 1-propanethiol sulfide	$CH_3SCH_2\text{-}CH_2\text{-}CH_2SH$	0.0004	0
Carbon disulfide	CS_2	0	0
Isopropyl mercaptan	$(CH_3)_2CHSH$	0	0
Ethyl methyl sulfide	$CH_3SCH_2CH_3$	0	0
Hydrogen sulfide	H_2S	0.1460	0
Carbonyl sulfide	COS	0	0.0287
Dimethyl sulfide	CH_3SCH_3	0	0

[a] Adapted from Lee (1975).

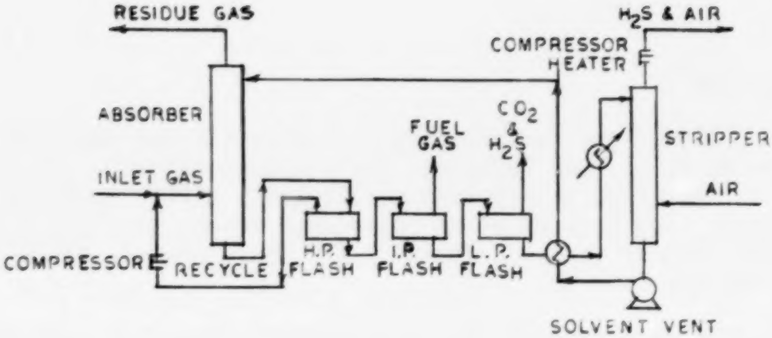

Figure 11. Selexol flow sheet for a gas containing large amounts of both H_2S and CO_2 (Maddox 1974).

Final Cleanup--
When gas must be treated by catalytic processes, even a few parts per million of sulfur may constitute a serious poison for the catalyst. For conventional methanation processes using nickel catalysts, catalyst life will be about 2 years when the gas contains 0.07 ppm sulfur; whereas a catalyst life of 5 years or more is expected for sulfur-free gas (Institute of Gas Technology 1972).

The Synthane process uses activated carbon for final sulfur cleanup (duplicate vessels so that one vessel can be taken offstream for regeneration).

According to the Institute of Gas Technology (1972), activated carbon which has been impregnated with certain metal oxides is used as a guard system to obtain very low sulfur concentrations. Hydrogen sulfide, carbonyl sulfide, carbon disulfide, thiophenes, and mercaptans are removed by the carbon (Table 22) as are any oils remaining in the gas. When the capacity of the bed is reached, the adsorber is removed from service and regenerated with steam and air. Some elemental sulfur formed during regeneration accumulates in the carbon pores, gradually deactivating the bed. After repeated adsorption-regeneration cycles, the impregnated carbon must be replaced with fresh adsorbent.

If the Synthane carbon is regenerated, the available flow diagrams indicate that regeneration steam and materials driven off the activated carbon are returned to the Benfield regenerator tower, where they commingle with other condensate from the regenerator and are sent to the decanter. At the Synthane Pilot Plant, the flow diagram would indicate that the carbon drum stripping steam and accompanying oil will indeed be routed to the Benfield absorbent regenerator overhead flux stream. It would appear that these light oils would not stay in the regenerator column, but would go with the acid gas stream to the Stretford unit.

The above estimates indicate that the gas feed to the activated carbon reactor will contain some light oil and some high molecular weight aromatic hydrocarbons. These would be concentrated in the activated carbon. It seems doubtful that the heavier material could be completely removed from the adsorbent.

METHANATION

General Discussion

The sweetened coal-derived synthesis gas contains a large quantity of carbon monoxide (low-Btu value) and hydrogen (low Btu/unit volume). In order for this gas to be brought up to pipeline quality, the carbon monoxide and the hydrogen contents must be reduced to low enough values to yield a product with a heating value greater than 900 Btu/cf. (The gas industry specifies that pipeline gas contain <0.1 vol % CO.)

To accomplish this objective all existing processes use the methanation reaction, which occurs in the presence of a catalyst, and combines carbon monoxide and hydrogen to produce methane and water:

$$CO + 3H_2 \xrightarrow[800^\circ \text{ to } 900^\circ F]{\text{high pressure}} CH_4 + H_2O$$

The methanation reaction is highly exothermic, liberating as much as 10% of the heating value of the total methane produced in the overall gasification process (Institute of Gas Technology 1974).

If the reaction temperature is allowed to rise above 900°F (482°C), carbon will be deposited from the breakdown of either the carbon monoxide or the methane (Moeller et al. 1974). Further, temperatures above 900°F will result in rapid catalyst deactivation.

The very large amount of heat released is a major problem in methanation. This heat must be removed while the temperature is maintained between the limits of 450°F (232°C) and 900°F (482°C) at all points in the system. The various processes differ in the methods they use to handle this problem (Institute of Gas Technology 1972).

Although the heats of reaction are not influenced greatly by temperature, changes in free energy and equilibrium constants for methanation reactions are quite sensitive to temperature. Thus, equilibrium methane yields are reduced critically at high temperatures, requiring that catalyst beds be operated at the lowest temperatures that are consistent with acceptable catalyst activity (Huffstetler and Rickert 1976).

Pressure does not appreciably affect methane yield until the temperature exceeds 942°F (506°C); above this temperature, increasing pressure tends to decrease the minimum hydrogen:carbon monoxide ratio required to prevent carbon deposition (Mills and Steffgen 1973).

Considerable research has been done on catalyst materials. Only five — ruthenium, nickel, cobalt, iron, and molybdenum — have been identified as having commercial importance (Strakey et al. 1975). Ruthenium is very active, but because it is relatively rare, there is a question as to whether the tonnages required for large-scale commercial use would be available (Huffstetler and Rickert 1976).

Nickel is inexpensive, very active, and highly selective to methane; thus, it is the catalyst of choice for most commercial operations. Cobalt is less active and less selective than nickel; iron is less active than cobalt and catalyzes carbon formation; molybdenum is of lower activity than iron, fairly selective, but it has the advantage of being resistant to sulfur (Huffstetler and Rickert 1976).

Commercial nickel catalysts consist of 25-77 wt % nickel on a high-surface area, refractory support such as kieselguhr or alumina. Raney nickel is also a widely used catalyst. This catalyst is formed by the leaching of the aluminum from an alloy, composed of 42 wt % nickel and 58 wt % aluminum, with sodium hydroxide. The result is a spongy skeletal catalyst that is very active in methanation (Huffstetler and Rickert 1976).

Catalyst deactivation, a severe problem in catalytic methanation, can occur through any of several mechanisms (Strakey et al. 1975):

1. $Ni + H_2S \longrightarrow NiS + H_2$

2. $Ni\ (75\ \text{Å}) \longrightarrow Ni\ (1000\ \text{Å})$

3. $2CO \longrightarrow C + CO_2$
   $CH_4 \longrightarrow C + 2H_2$

4. $3Ni + 2CO \longrightarrow Ni_3C + CO_2$
   $3Ni + CH \longrightarrow Ni_3C + 2H_2$

5. $Ni + 4CO \longrightarrow Ni(CO)_4$

6. $Fe(CO)_5 \longrightarrow Fe + 5CO$

Reaction 1, the poisoning of the catalyst by sulfur, is common to all metallic catalysts except molybdenum. Strakey et al. (1975) tried to keep sulfur concentration below 0.1 ppm to avoid irreversible contamination.

The sintering effect is represented by reaction 2. It is generally known that, at temperatures above 842°F (450°C), nickel crystallites grow in size and a loss of surface area leads to reduced catalytic activity. Reaction 3 is the Boudouard reaction in which elemental carbon is formed by heterogeneous decomposition of CO or CH_4 during methane synthesis. Nickel carbide forms as a result of reaction 4. This reaction deactivates the catalyst material, but is reversible; treatment with hydrogen at >482°F (250°C) will reactivate a nickel carbide-deactivated catalyst (Strakey et al. 1975). A potentially serious reaction is the one that forms nickel carbonyl (reaction 5). Because this reaction occurs only at low temperatures, it is avoided by contacting the catalyst with synthesis gas at temperatures above 500°F (260°C) and maintaining that temperature until all carbon monoxide has been purged from the system (Huffstetler and Rickert 1976).

The final reaction, 6, is one that has its beginnings outside the reactor vessel. Iron carbonyl can form when carbon monoxide reacts, at high pressure and low temperature (212° to 392°F [100° to 200°C]), with carbon steel piping.

The iron carbonyl is carried into the reactor, where it decomposes according to reaction 6 and effectively deactivates the nickel catalyst by forming iron deposits. Choosing less reactive piping material, such as stainless steel, will prevent the reaction from occurring (Strakey et al. 1975).

Process Discussion

The tube wall reactor (TWR) methanator and the hot gas recyle (HGR) methanator, both designed by the U.S. Bureau of Mines, are being tested at the Synthane Pilot Plant. In most methanation systems, the heat of reaction is removed from the reactor as sensible heat in the gas. The TWR (Figure 12) methanation system involves removing the heat of reaction directly from the catalyst surface. An alloy of nickel and aluminum is flame-sprayed on the inner surface of the tubes. Treatment with caustic removes the aluminum, leaving a highly active Raney-nickel catalytic surface. The fresh feed gas enters the reactor and reacts on the catalytic surface of the tubes. The heat flows from the nickel surface through the tube wall to boiling Dowtherm A on the shell side. The temperature on the inside tube wall is held at the desired level by controlling the pressure at which Dowtherm is boiling.

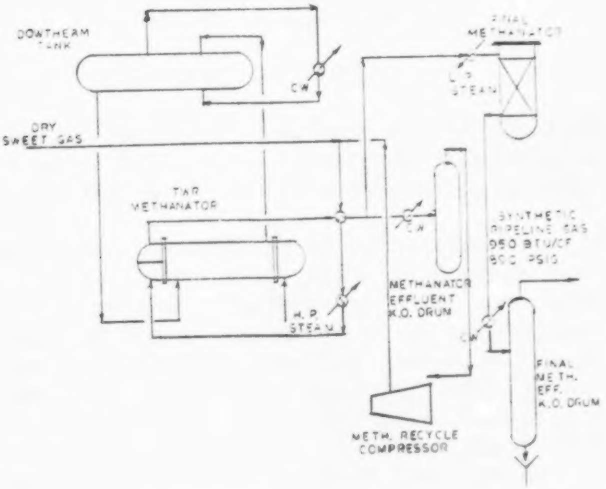
DOWTHEAM TANK
CW
FINAL METHANATOR
L.P. STEAM
DRY SWEET GAS
TWR METHANATOR
CW
SYNTHETIC PIPELINE GAS
950 BTU/CF
900 PSIG
METHANATOR EFFLUENT K.O. DRUM
H.P. STEAM
CW
FINAL METH. EFF. K.O. DRUM
METH. RECYCLE COMPRESSOR

Figure 12. Tube wall reactor methanation — Synthane Pilot Plant.

The HGR methanator (Figure 13) is a simpler system. Product gas is recycled back to the inlet of the reactor to dilute the feed and to reduce the CO concentration so that a conversion of about 2% CO is obtained in the reactor. Thus, with an inlet temperature of 572°F (300°C), the exit temperature does not exceed 750°F (400°C). These limits apply to the Raney nickel catalyst. Other catalysts are claimed to operate at higher temperatures. In the original bench facility, a feed gas containing about 23% CO with an H_2:CO ratio slightly in excess of 3:1 was used, for which the required recycle volume is 10 times the feed volume (10:1). If all this recycle were returned hot so that no moisture was removed, the steam concentration would approach 50%, which is undesirable from an equilibrium standpoint and may cause catalyst oxidation. Therefore, 30% of the recyle stream is cooled to room temperature and water is condensed. Thus, a 7:1 hot recycle ratio and a 3:1 cold recycle ratio are used (Strakey et al. 1975).

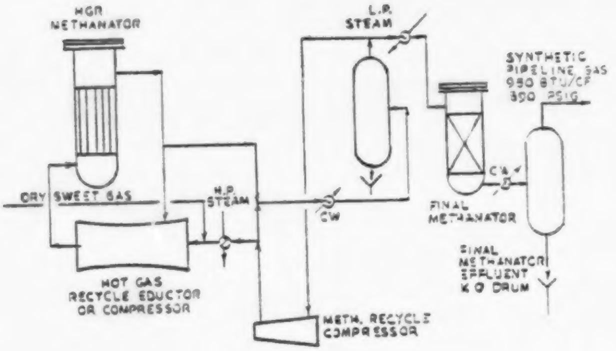

Figure 13. Hot gas recycle methanation — Synthane Pilot Plant.

Of special interest is the low pressure drop through the HGR unit, which is only 0.3% of that through a pelleted catalyst bed. This low pressure drop is a result of applying the catalyst to flat plates that are arranged in parallel and stacked in bundles in the HGR. Flame spraying or metallizing is used to deposit the catalyst. For the HGR plates, Raney nickel alloy powder (80 to 200 mesh) is fed through a hydrogen-oxygen flame, where it partially melts and solidifies on the surface of the flat plate. This process is normally used to apply corrosion resistant coatings, for hard-facing soft metals with hard coatings, and to build up worn journals. First, a bond coat, .006" thick, containing 95% Ni and 5% Al, is applied to the stainless steel substrate to improve adhesion, and then a coating of Raney nickel, .019" thick, is sprayed onto the plate. The plate is then activated by caustic leaching and kept under hydrogen until it contacts the SYNGAS at an elevated temperature (Strakey et al. 1975).

After this first-stage methanation, the cold (107°F [42°C]) product gas is heated to 600°F (316°C) and then passed through a final, or polishing, packed-bed methanator. The final product gas is 89.6 vol % methane. This gas is sampled and then burned in the thermal oxidizer (Institute of Gas Technology 1972; U.S. Bureau of Mines 1972).

Special Cases--
The Bituminous Coal Research, Inc.,(BCR)-developed fluidized bed catalytic methanation reactor is being tested at the Bi-Gas plant. As stated previously, the fluidized bed offers far better heat-transfer capabilities than are possible with fixed-bed reactors. The BCR unit is designed with sufficient internal cooling coils and heat-exchange capacity to control the exothermic heat of methanation at higher levels of carbon monoxide concentrations in the feed gas than is possible with fixed beds (Evans 1976c).

The CO_2 Acceptor uses the heat extraction method of methanation. Here, heat-exchanger tubes are packed with a pelleted catalyst. Boiling Dowtherm on the shell side of the exchanger removes the heat and the hot Dowtherm is used to raise high-pressure steam (Strakey et al. 1975).

The original methanation system used at the HYGAS Pilot Plant was a combination of the cold quenching and recycle systems. In this system, fresh feed is mixed with recycle gas in order to (1) dilute the feed to maintain as low a temperature as possible in the reactor and (2) act as a coolant for the gas stream itself. In practice, a portion of the coal-feed gas is mixed with hot recycle gas and then fed to the first catalyst bed. The hot gas from the first reactor is mixed with recycle gas from the second reactor and/or more fresh sweet gas. It is cooled further if necessary and reacted in a second catalyst bed. A portion of the gas product is cooled and passed through a final catalyst bed to insure maximum conversion. Gas temperatures vary from a 550°F (288°C) feed temperature to 800°F (427°C) outlet temperature. In this way the overall recycle ratio and pressure drop can be significantly reduced. More recently, a carbon guard system for removal of sulfur compounds has been installed upstream of the methanation unit (Evans 1976d).

In October of 1976, a skid-mounted liquid phase methanation process unit developed by Chem Systems, Inc., was installed at the HYGAS plant. This unit was to have been brought onstream in March of 1977. In this process, inert liquid (either a paraffinic or aromatic oil — WITCO 40 mineral oil has been used) is pumped upward through the reactor, which operates at 1000 psig and 570°F (300°C), at a velocity sufficient both to fluidize the catalyst and to remove the reaction heat. At the same time, the sweet feed gas is passed upward through the reactor, where it is converted to methane in the presence of the fluidized nickel catalyst. (Calsicate Ni-2305 has been tested.) The heat of the exothermic reaction is adsorbed by the inert liquid as sensible heat. The liquid is then circulated through an external heat exchanger to maintain the desired temperature, and the cooled inert liquid stream is recycled to the reactor.

The product gas leaving the top of the reactor contains 95% to 99.5% methane, depending on the pressure, temperature, and flow rate of the inlet gas. Other components of the product gas are water vapor and vaporized inert liquid, along with minute quantities of ethane, propane, hydrogen, and carbon dioxide. Most of the inert liquid condenses in the primary cooler; the remainder condenses in the secondary cooler along with the water. The inert liquid and water are separated; the inert liquid is recycled to the methanator and oily water is sent to the incinerator. No recycle is required as the reaction is nearly complete in one pass, and the product is high-Btu synthetic natural gas (U.S. Energy Research and Development Administration 1976b).

Problems--
Each of the above described systems may develop its own operating problems of plugged bed or lines, leaking valves, or leaking pumps. The leaks will release carbon monoxide, methane, and hydrogen into the workplace. However, the frequency and severity of these leaks should be far less than in the upstream portion of the plant.

The formation of nickel carbonyl is of concern. Again, as long as the proper operating procedures are followed, few if any problems should develop. Operating personnel at the HYGAS Pilot Plant state that they have been concerned about this problem, but that they have seen no signs of catalyst deactivation, such as reduction in gas quality out of the vessel or change in the temperature pattern within the reactor bed. Catalyst deactivation would be the first sign of nickel carbonyl formation (oral communication, November 9, 1976, with W. G. Baer, HYGAS Pilot Plant, Institute of Gas Technology, I.T.T. Center, 3424 South State Street, Chicago, Illinois 60616). It has been suggested that nickel carbonyl formation could occur at the cold surfaces of the heat-transfer piping in the fluid-bed, liquid phase methanation unit, depending upon the pipe surface temperature. However, since nickel carbonyl does dissociate at the normal methanation temperatures at which the fluid bed is operated, one would expect the chances of escape of the nickel carbonyl from the reactor to be minimal.

In case of an operating problem in this or any gas purification system, the product gas can be diverted directly to the thermal oxidizer until the problem is eliminated.

ACID GAS TREATMENT

The acid gas from the Synthane Pilot Plant's hot carbonate regenerator (Figure 14) contains carbon dioxide, hydrogen sulfide, and water, as shown in Table 23. This acid gas may contain some light oil as already indicated. The light oil should pass through the absorbers with the carbon dioxide and other hydrocarbon gases. The composition of the desulfurized acid gas will approximate that shown in Table 24. At Synthane, this desulfurized acid gas may be thermally oxidized or recycled as inert gas in other parts of the plant. The composite molten sulfur analysis from the Stretford unit will approximate that shown in the second column of Table 24.

At the Bi-Gas Pilot Plant, a commercially available skid-mounted Claus unit will be used to treat the acid gas. This unit will also produce a molten sulfur, which can be pumped into a truck for disposal.

Table 23. Acid gas feed compositions to sulfur removal unit.

	Synthane[a]	HYGAS
Gas Components, mol %	Bituminous Coal	Run 37, Montana Lignite[b]
Hydrogen	0.49	3.57
Carbon Monoxide	0.06	0
Carbon Dioxide	87.65	93.24
Methane	0.31	1.71
Ethane	ND[c]	0.12
Hydrogen Sulfide	1.59	0.10
Water	9.90	ND
Nitrogen	ND	1.26

[a] Based on process flow diagram calculations, not on pilot plant data (U.S. Bureau of Mines 1972).

[b] Dry basis (Lee 1975).

[c] No data.

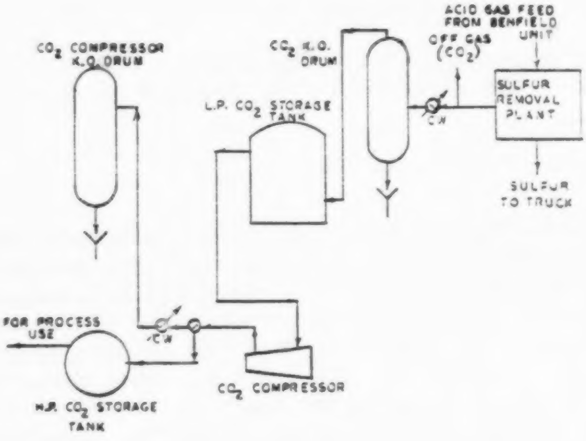
ACID GAS FEED FROM BENFIELD UNIT
OFF GAS (CO_2)
CO_2 COMPRESSOR K.O. DRUM
CO_2 K.O. DRUM
L.P. CO_2 STORAGE TANK
SULFUR REMOVAL PLANT
C.W
SULFUR TO TRUCK
FOR PROCESS USE
C.W
CO_2 COMPRESSOR
H.P. CO_2 STORAGE TANK

Figure 14. Acid gas processing — Synthane Pilot Plant.

Table 24. Synthane sulfur removal plant product.[a]

Components, mol %	CO_2 Recycle and/or Off-gas to Thermal Oxidizer	Sulfur to Disposal
Hydrogen	0.51	ND
Carbon Monoxide	0.06	ND
Carbon Dioxide	91.76	ND
Methane	0.32	ND
Hydrogen Sulfide	(150 ppm)	ND
Water	7.35	2.1
Sulfur	ND	97.9

[a] Adapted from U.S. Bureau of Mines (1972).

Claus Process

The Claus process (Figure 15) is an essentially atmospheric pressure process operating basically in the following manner.

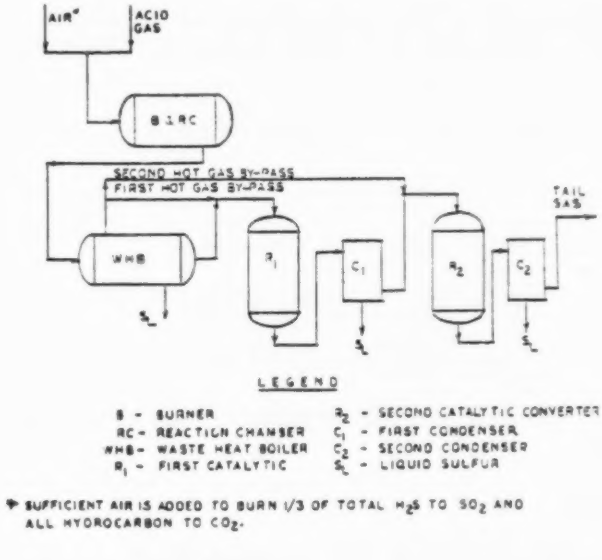
AIR*
ACID GAS
B & RC
SECOND HOT GAS BY-PASS
FIRST HOT GAS BY-PASS
WHB
S_L
R_1
C_1
R_2
C_2
TAIL GAS
LEGEND
B - BURNER
RC - REACTION CHAMBER
WHB - WASTE HEAT BOILER
R_1 - FIRST CATALYTIC
R_2 - SECOND CATALYTIC CONVERTER
C_1 - FIRST CONDENSER
C_2 - SECOND CONDENSER
S_L - LIQUID SULFUR
* SUFFICIENT AIR IS ADDED TO BURN 1/3 OF TOTAL H_2S TO SO_2 AND ALL HYDROCARBON TO CO_2.

Figure 15. Claus "once through" process flow scheme (Maddox 1974).

The acid gas, containing 15 to 90 mol % H_2S (Beers 1973) is combined with sufficient air to burn one-third of the total H_2S to SO_2 and all of the hydrocarbons to CO_2. (Alternatively, one-third of the total acid gas is burned, then recombined with the unburned gas.) A part of the hot gas is cooled and a portion bypasses the coolers so that the reactor temperatures can be maintained. (Each reactor inlet temperature must be above the sulfur dew point, preferably 450°F [232°C], to avoid condensation of the liquid sulfur in the catalyst bed. Condensation could cause plugging and catalyst deactivation.)

In the reactor the SO_2 and H_2S react to form sulfur.

$$2H_2S + SO_2 \xrightarrow[700^\circ \text{ to } 750^\circ F]{\text{Bauxite catalyst}} 1.5S_2 + \text{steam}$$

From the catalytic reactor the hot gases flow into the condenser, where they are cooled to 300°F (149°C) and the liquid sulfur is removed. Sulfur must be removed from the condenser in the 300°F range. (Because of a phase change at 320°F (160°C), the viscosity of liquid sulfur increases rapidly with increasing temperature and could not be removed from the condenser.) Cooled gases can then be recombined with a second hot gas bypass flow to balance temperatures at the entrance of the second reactor inlet. Product gas should contain only 0.5% to 10% of the H_2S fed into the unit (Maddox 1974). This composition is acceptable in the pilot plant situation.

Claus reaction variations accommodate the various concentrations of acid gas feeds, with the optimum Claus process depending primarily on the hydrogen sulfide concentration in the feed (Dailey 1976).

Problems--
Hydrocarbon in the feed to the Claus unit causes an increase in undesirable side reaction products. Following are some of the possible reactions (Maddox 1974):

$$CH_4 + SO_2 \longrightarrow COS + H_2O + H_2$$

$$CO + S \longrightarrow COS$$

$$CO_2 + H_2S \longrightarrow COS + H_2O$$

$$CH_4 + 2S_2 \longrightarrow CS_2 + 2H_2S$$

$$2CO + S_2 \longrightarrow CO_2 + CS_2$$

Should this unit prove inoperable, the regenerator acid off-gas will be sent to the thermal oxidizer.

Holmes-Stretford Process

The Holmes-Stretford process (Figure 16) is capable of operating on acid gases containing only low concentrations of H_2S.

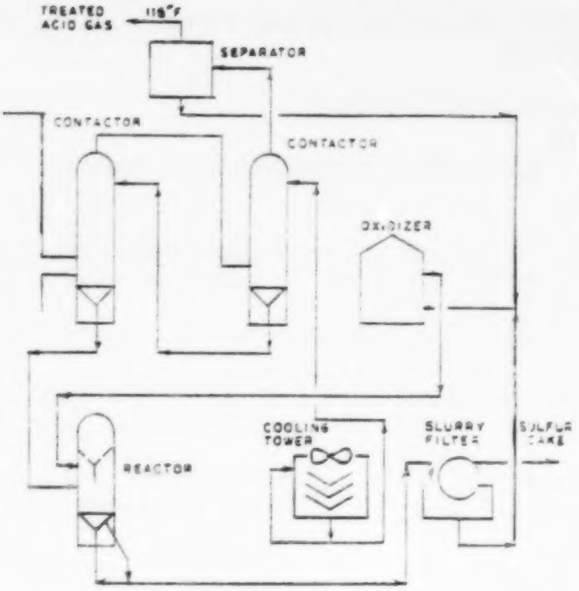

Figure 16. Holmes-Stretford sulfur recovery — Synthane Pilot Plant.

In this process, the 120°F (49°C) acid gas is washed countercurrently by sodium vanadate containing the sodium salt of anthraquinone disulfonic acid (ADA) as an activator. The hydrogen sulfide in the acid gas reacts with the vanadate to form sulfur.

$$4NaVO_3 + 2H_2S \xrightarrow{pH\ 9} Na_2V_4O_9 + 2S + 2NaOH + H_2O$$

The reduced vanadate is then oxidized by the ADA, which in turn is reoxidized in the atmospheric air. This is done in an oxidizer vessel by air spraying. The air also acts as a flotation agent in frothing out the fine grained sulfur product. The slurry of solid sulfur is filtered; the filtrate is returned to the process; and the sulfur is collected in a molten sulfur storage tank (Maddox 1974; Institute of Gas Technology 1972; Vasan and Willett 1976).

There is a by-product conversion of H_2S into thiosulfate. Through proper design and the use of special additives this conversion into thiosulfate can be kept down to the 1% to 2% level. Accumulated thiosulfate must be purged.

UTILITIES

The coal gasification pilot plants require a substantial utility section including facilities for:

- Water demineralization
- Water treating to boiler feed water specifications
- Potable water supply

- Steam production (with natural gas or oil fired boilers)
- Water for fire fighting
- Cooling water supply
- Cooling water anticorrosion treatment
- Cooling water towers
- Air compression and drying (for instrument air supply)
- Thermal oxidation
- Wastewater ponds
- Emergency power generation (diesel or propane generator supplying sufficient power to permit the plant to shut down safely under emergency conditions)
- Compressed or liquid gas storage such as carbon dioxide, oxygen, and/or nitrogen
- Inert gas generation and compression such as carbon dioxide
- Electrical power conversion and transmission to the plant workplace

These utilities are similar to those in most commercial facilities. In general, these functions are generally located within or near to a single building and are noisy.

OTHER FACILITIES

There are other operating facilities within the plant for maintenance, instrumentation, and laboratory analysis. The maintenance force may be large enough to cover all operating and maintenance requirements, or it may be only large enough to cover maintenance problems in rotating equipment, such as centrifugal and reciprocating pumps and compressors. At the HYGAS plant, maintenance is concerned only with the rotating equipment. In this latter case, regular inspection and cleaning of vessels are performed by the operating crew, while major maintenance functions are contracted to commercial firms. At the Synthane plant, all maintenance functions are carried out by an outside contractor, while at the CO_2 Acceptor plant, all maintenance is done by the plant maintenance force.

Analytical functions are relatively simple and may be confined to the definition of major process components as required for plant operation. In general, facilities other than gas chromatographs for routine gas or liquid analyses are not available. Detailed analyses must be performed in an outside laboratory. In some cases, the analysts also do the plant sampling during plant operations (HYGAS). This crew is then exposed to emissions which may accompany the sampling procedure from the entire workplace for most of the workday in addition to say other hazards in the workplace.

HEALTH EFFECTS

This chapter reviews the health effects that might ensue if workers were exposed to the process stream and waste chemical hazards identified in the process discussion of coal gasification and Appendix A; it also reviews potential physical stresses. Its purpose is to support recommendations for protection of workers and to provide a convenient source of information for those responsible for the protection of workers' health. Description of an effect does not imply that workers will necessarily be at risk in any particular coal gasification pilot plant. Assessment of that risk requires knowledge also of likelihood of exposure, and such knowledge is at present incomplete.

TOXIC EFFECTS

"Toxic" here includes "carcinogenic," although the terms are often separated. Chemical carcinogenesis can be regarded as "a very special aspect of an adverse toxicologic reaction." (Weisburger 1975)

Sources of data include toxicologic experiments and epidemiologic studies. Animals have been exposed in the toxicology laboratory, usually to single substances or to simple mixtures and occasionally to complex coal products. Epidemiologic studies have been performed on humans who have worked in coal processing plants, but — in contrast to the laboratory — exposure there is uncontrolled and difficult to estimate.

A special characteristic of coal gasification plants is that any occupational exposures occurring therein are likely to be to complex mixtures of chemicals. If the chemicals are similar in constitution and toxicologic mechanism, the total effect might be simply additive, and it might then be calculable in the same manner as is recommended by the American Conference of Governmental Industrial Hygienists (1976) for the estimation of threshold limits for exposure to such mixtures: If the sum of the fractions, (observed concentration)/(threshold limit), for each component is more than unity, the limit is exceeded. Synergistic action (i.e., combined effect exceeding the sum of individual effects) may occur and this is particularly significant with carcinogens. Other chemicals, not carcinogenic of themselves, can enhance the potency of carcinogens or can promote tumor formation even long after application of the carcinogen. Carcinogenic potency can also be decreased, as in the application of weak carcinogens such as dibenz(*a,g*)fluorene and chrysene together with strong carcinogens such as benzo[*a*]pyrene (B*a*P). Finally, if components act independently, each can be considered as though the others were not present. This is seen with some carcinogens and with other toxicants; e.g., in concurrent exposure to an azo dye that induces liver tumors and 4-dimethylaminostilbene, which affects the ear duct (Weisburger 1975).

There are several practical consequences of exposure to complex multiagent hazards. Complete chemical characterization of exposure hazards may be difficult or impossible, and even if a full analysis were available, the total effect would generally be unpredictable. It is clear also that the use of a single component of exposure as an index of total exposure — e.g., BαP as an index of total polycyclic aromatic hydrocarbons — must be viewed with caution.

The first evidence of health effects presented here is from studies of coal conversion workers and their environments; evidence is next presented for similar working environments such as coke ovens. The remainder of the evidence comes from observations on humans in quite different circumstances or from animal experiments.

Evidence of Health Effects from Coal Conversion Plants

Large-scale plants for coal conversion were constructed in Germany in the 1920's, in Great Britain in the 1930's, and in South Africa in the 1950's; pilot plant work began in the United States in the 1950's. The American experience provides the best available evidence of effects in man; it has been reported principally in a series of reports that appeared in the Archives of Environmental Health in 1960 (see below), relating to a pilot plant operated from 1952 through the late 1960's.

Sexton (1960a) stated that it was known that the plant would generate a wide range of chemicals, many of which could present acute or chronic toxic hazards. Examples of the expected compounds were aliphatic hydrocarbons, single-ring aromatics, polynuclear aromatics, phenols, aromatic amines, and N-heterocyclic aromatics. Sexton also stated that most of the hazards did not occasion great concern with the available controls in force but special attention was given to the presence of "at least one high boiling polycyclic aromatic chemical which is known to be carcinogenic." A toxicological investigation confirmed the cancer hazard (Weil and Condra 1960) and an industrial hygiene investigation (Ketcham and Norton 1960), concentrating on airborne material and skin contamination, established the etiology of skin contamination and resulted in recommendations for its abatement.

The medical report stated that:

> "In reporting the clinical effects in a group of 359 coal hydrogenation workers who were examined regularly over a 5-year period, it was found that the exposure of these men varied from several months to 23 years, and all of the lesions of significance were discovered in those workmen with less than 10 years' exposure. Those employees with more than 10 years' exposure obtained much of this in small experimental or laboratory-sized operations, and the exact extent of their exposure is not known. Those with skin lesions probably had much heavier exposures, although they were obtained over a shorter period of time. During the 5-year examination period, 63 skin abnormalities were discovered in 51 of the men. Of the 60 lesions excised, 55 tumors were subjected to histological study by local pathologists. Eleven of these lesions were diagnosed as skin cancers by either clinicians or pathologists, but the pathologist

> who reviewed the sections at a later date believed that only five of these were epitheliomas. The incidence of cancer in these men was between 16 and 37 times that reported in the literature. There were 54 suspected precancerous lesions of the skin, and 42 of these were verified as precursors of skin cancer by several pathologists."

Among the conclusions reached by these investigators were:

> "3. Heavy exposures to coal hydrogenation materials, even those of relatively short duration (less than 10 years) are capable of producing cutaneous tumors — both precursors and neoplasms.
>
> "4. The incidence of skin cancer in workmen exposed to the coal hydrogenation process in one plant is many times greater than that of West Virginia or the United States as a whole."

An association of coal hydrogenation with skin cancer was thus indicated, and Weil and Condra (1960) suggested its cause. They found, in mouse skin assays, that:

> "The light and heavy oil products were mildly tumorigenic. The light oil stream, boiling below 260°C, and its derivatives were without tumorigenic action. The streams boiling at higher temperatures, middle oil, light oil stream residue, pasting oil, and pitch product, were all highly carcinogenic, the degree of carcinogenicity increasing and the length of the median latent periods decreasing as boiling points rose."

The results are summarized in Figure 17.

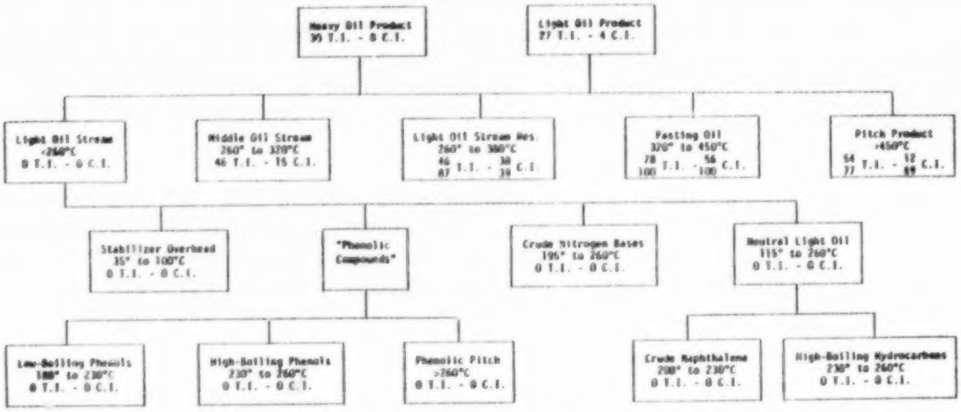
Heavy Oil Product
35 T.I. - 0 C.I.
Light Oil Product
27 T.I. - 4 C.I.
Light Oil Stream
<260°C
0 T.I. - 0 C.I.
Middle Oil Stream
260° to 320°C
46 T.I. - 15 C.I.
Light Oil Stream Res.
260° to 380°C
$\frac{46}{87}$ T.I. - $\frac{38}{39}$ C.I.
Pasting Oil
320° to 450°C
$\frac{78}{100}$ T.I. - $\frac{56}{100}$ C.I.
Pitch Product
>450°C
$\frac{54}{77}$ T.I. - $\frac{12}{69}$ C.I.
Stabilizer Overhead
35° to 100°C
0 T.I. - 0 C.I.
"Phenolic Compounds"
Crude Nitrogen Bases
195° to 260°C
0 T.I. - 0 C.I.
Neutral Light Oil
115° to 260°C
0 T.I. - 0 C.I.
Low-Boiling Phenols
180° to 230°C
0 T.I. - 0 C.I.
High-Boiling Phenols
230° to 260°C
0 T.I. - 0 C.I.
Phenolic Pitch
>260°C
0 T.I. - 0 C.I.
Crude Naphthalene
200° to 230°C
0 T.I. - 0 C.I.
High-Boiling Hydrocarbons
230° to 260°C
0 T.I. - 0 C.I.

Figure 17. Products and their carcinogenicity summarized.[a]

T.I. = Tumor index, mice with tumors as a percentage of total mice exposed after subtracting mice that died without tumor.

C.I. = Cancer index, similarly defined.

[a] Weil and Condra, 1960.

In the industrial hygiene study (Ketcham and Norton 1960) benzo[*a*]pyrene was used as a proxy for this group of chemicals because it was known as a potent carcinogen and was present in all of the middle oil and heavy oil fractions. Most of the air samples collected at the facility showed concentrations of the same order as that of large-city air, a few micrograms per 100 m^3. Some, taken close to particular operations, showed several hundred micrograms, or even over 1000 μg per 100 m^3. There was, however, no opportunity to establish any quantitative relationship with either observed skin contamination or skin cancer incidence.

No other reports of positive evidence of increased skin cancer incidence in coal conversion plants have been found in the United States, nor has any evidence for other specific effects been found. It is clear, however, that this does not dispose of the hazards. A recent examination of a pilot plant by ultraviolet light showed extensive surface contamination, which very probably contained carcinogenic hydrocarbons (Bolton 1976).

The absence of reported lung cancer is similarly no cause for complacency. For example, high airborne concentrations of B*a*P were reported in some circumstances as already noted (Ketcham and Norton 1960), and the fact that only skin cancer was observed may have been due to the long induction period for lung cancer (Hueper 1952) and lack of adequate follow-up. In this connection, a paper by Holmes et al. (1970) presents "evidence of an increased risk of subsequent primary cancer in the respiratory and upper digestive tracts of men who have had epithelioma of the scrotum...." The same may be true of skin cancer generally.

Evidence of Health Effects from Similar Plants

Gasworks, where coal is heated in retorts with the primary purpose of producing flammable gas, or coke ovens, where the coke is the primary product, have provided much more evidence of associated health effects than coal conversion plants, and some of it is quantitative. It should be noted, however, that this evidence does not imply comparable levels of hazard in coal conversion. Gasworks and coking plants heat the coal with minimal containment. Conversion plants typically operate at high pressure as well as high temperature, and therefore necessarily with good containment in normal operating conditions. The nature of the toxic hazards and their amounts within the various process streams are similar: the likelihood of exposure is however less at conversion plants.

Producer gas plants have features in common with coke ovens and gasworks on the one hand and with coal conversion on the other; and studies of producer gas workers provided the first evidence of increased lung cancer incidence (Kuroda and Kawahata 1936). Later evidence showed a mortality rate from lung cancer 33 times that of control workers from the same steelworks (Kawai et al. 1967).

In a British study (Doll et al. 1965) over 11,000 gasworkers and pensioners were observed for an 8-year period and over 3,000 of them were followed for a further 6 years as part of another study (Doll et al. 1972). In the 12-year period lung cancer deaths were higher by 140% and bladder cancer deaths by 208% in men heavily exposed to the products of coal carbonization as compared with those exposed only to by-products. Analysis of gasworks air (Lawther et al. 1965) showed a general level of about 3 μg per m^3 of benzo[*a*]pyrene (100 times that in typical London air) and over 200 μg per m^3 in the worst working area. The tarry particles were in the respirable size range, mostly 1 μ and below and therefore capable of penetrating the deep lung, although not being completely retained. These reports clearly established a relationship of illness with exposure at gasworks but did not provide a quantitative dose-response relationship.

Coke oven studies provided similar evidence. Studies initiated in 1962 in Allegheny County, Pennsylvania, (and later extended: Fannick et al. 1972) were reported in 1970-1972 (Lloyd et al. 1970; Lloyd 1971; Redmond et al. 1972). These showed a strong association of excess deaths from respiratory and urogenital neoplasia with both intensity of exposure and length of employment. Tables 25 and 26 are extracted from this work and Table 27 shows the relative levels of exposure of topside workers and two categories

Table 25. Relative risk of death for selected causes by coke oven subdivisions for coke oven workers (1961-1966).[a]

	Full topside	Partial topside	Side oven
Cause of death	Relative risk	Relative risk	Relative risk
All causes	1.12	1.07	0.92
Malignant neoplasms — lung, bronchus, and trachea	7.24	2.14	1.73
Malignant neoplasms — genitourinary system	*b*	*b*	2.02
Other malignant neoplasms	0.86	0.44	0.79
Tuberculosis of the respiratory system	*b*	*b*	1.06
Other diseases of the respiratory system	0.99	1.78	1.01
Cardiovascular renal diseases	0.84	1.18	0.80
Accidents	0.72	0.94	1.19
All other causes	1.00	0.76	0.85

[a] Adapted from the work of Redmond et al. (1972).
[b] Less than 5 deaths observed.

Table 26. Relative risk of death for selected causes by length of employment at entry to study for coke oven workers.[a]

	5 years or more at coke oven	Less than 5 years at coke oven
Cause of death	Relative risk	Relative risk
All causes	1.08	0.83
Malignant neoplasms — lung, bronchus, and trachea	3.48	1.70
Malignant neoplasms — genitourinary organs	2.01	*b*
Other malignant neoplasms	0.93	0.40
Tuberculosis of the respiratory system	1.00	*b*
Other diseases of the respiratory system	1.28	0.88
Cardiovascular renal diseases	0.90	0.79
Accidents	0.88	1.12
All other causes	0.94	0.77

[a] Adapted from the work of Redmond et al. (1972).
[b] Less than 5 deaths observed.

Table 27. Mean level of coal tar pitch volatiles (mg/m^3).[a]

Exposure group	Average CTPV (mg/m^3)
Topside	3.15
Side oven 1	1.99
Side oven 2	0.88

[a] Adapted from the work of Mazumdar et al. (1975).

of side oven workers (Mazumdar et al. 1975). Mazumdar et al. concluded that the Threshold Limit Value (TLV) recommended by ACGIH, 0.2 mg/m^3 coal tar pitch volatiles in total particulates, was acceptable because their analysis indicated that exposure at this level for an average of 30 years did not increase the risk of death from lung cancer.

The ACGIH TLV of 0.2 mg/m^3 was first adopted in 1967 and it was subsequently adopted as a Federal standard under the Occupational Safety and Health Act of 1970. The standard (29 CFR 1910) refers specifically to anthracene, B*a*P, phenanthrene, acridine, chrysene, and pyrene, and a note on interpretation says that "coal tar pitch volatiles include the fused polycyclic hydrocarbons which volatilize from the distillation residues of coal, petroleum, wood, and other organic matter."

The NIOSH criteria document for coke oven emissions (National Institute for Occupational Safety and Health 1973a) remarked of the TLV and Federal standard that "in the absence of information on a safe level, this environmental standard can be considered only an index of worker exposure." NIOSH also noted that the benzene soluble fraction of total particulates may be a questionable index of health hazard because (1) irritants may enhance carcinogenicity and (2) respiratory protection against gases may be needed.

In 1974 the U.S. Department of Labor (OSHA) established a Standards Advisory Committee on Coke Oven Emissions. A proposed standard of 300 μg of respirable particulate matter per cubic meter of air was published in 1965 and a new standard for worker exposure to coke oven emissions was promulgated in 1976 (Federal Register 1976), which became effective on January 20, 1977. Exposure is limited to 150 μg of benzene soluble fraction of total particulate matter (BSFTPM) per cubic meter of air, averaged over an 8-hour period. OSHA found the BSFTPM to be a "more specific measure of exposure to the carcinogenic components of coke oven emissions than either respirable or total particulate matter. The benzene soluble fraction of total particulate matter sampling is less likely than sampling of other indicator substances to be affected by interference from emissions present but not generated from the destructive distillation of coal."

Other Evidence of Health Effects

Additional evidence of health effects is derived from observation of humans in circumstances quite different from those at coal conversion plants or from animal experiments. In comparison with the previous evidence, the available data are abundant and generally much more precise, but they are necessarily derived from conditions that are more remote, inferentially, from those of direct concern. Most of the evidence is experimental and comes from controlled exposures to single substances or to very simple combinations of substances.

The evidence is presented very briefly in relation to individual chemicals or closely related groups of chemicals selected from the process stream components and possible emissions described in the process discussion of coal gasification and listed in Appendix A. The selection was based on potential hazards as indicated by specific toxicity and estimated probability of worker exposure in normal operations and maintenance.

The chemicals are arranged alphabetically. Some are treated individually, while others are treated as groups which are similar in toxic effects and chemical properties. To help in locating information, a list is provided below.

Aliphatic hydrocarbons
Ammonia
Aromatic amines
Aromatic hydrocarbons — see also Polycyclic aromatic hydrocarbons
Arsine — see under Trace elements, Arsenic
Carbon disulfide
Carbon monoxide
Carbonyl sulfide
Heterocyclic aromatics
Hydrogen chloride
Hydrogen cyanide
Hydrogen sulfide
Mineral dust and ash — see also Trace elements
Nickel carbonyl
Nitrogen oxides
Nitrosamines
Phenols
Polycyclic aromatic hydrocarbons
Sulfur oxides
Trace elements

The information is presented on the basis of relevance to other chapters of this report:

- Toxic effects are of interest to those involved with medical monitoring. The emphasis is on chronic exposure and the organs affected: i.e., "what to look for."

- Occupational (OSHA) standards or other indicators of "safe" levels of exposure are useful in selecting workplace monitoring requirements and controls.

- Physical properties — physical state at ambient temperatures and boiling point if normally liquid or solid — determine the type of exposure and consequent requirements for personal protective equipment. They also affect workplace monitoring and engineering control requirements.

Aliphatic Hydrocarbons--
This group in general is unlikely to present a significant hazard at coal gasification plants because any probable exposure will be to gas or vapor at concentrations far below toxic levels. There is one notable exception: dodecane, a liquid boiling at 421°F (216°C). It is not highly toxic but it is a remarkable potentiator of skin tumorigenesis by B*a*P, lowering the threshold dose in experiments by Bingham and Falk (1969) by a factor of 10^4, and it is a known product of low-temperature coal conversion. It accordingly has a special status as a target for investigation and as a signal for protective action. It presents a suspected but unproven inhalation hazard as a carcinogen, as well as the proven contact hazard.

Ammonia--
This gas is very soluble in water. It is so intensely irritating that an acutely toxic dose cannot voluntarily be inhaled. There is no evidence of ill effects from prolonged workplace exposure at tolerable concentrations.

The OSHA standard is a time-weighted average (TWA) concentration of 50 ppm. NIOSH has recommended a 50 ppm/5 min ceiling limit.

Aromatic Amines--
These liquids or solids have moderate to high boiling points. Aniline and other substituted benzenes are highly toxic, causing methemoglobinemia, central nervous system effects, liver damage, and skin sensitization. The fused two-ring β-napththylamine and the biphenyl benzidene are potent carcinogens, especially the former which has been shown to be associated with excess bladder cancer in gasworkers (Doll et al. 1965).

The OSHA standard for aniline and similar compounds (toluidine, xylidine) is a time-weighted average concentration limit of 5 ppm; β-naphthylamine and benzidine are regulated by engineering controls and work practices, not by exposure limits.

Aromatic Hydrocarbons (other than polycyclics)--
These are liquids and solids of moderate to high boiling point. Vapor hazards are likely only with benzene and related compounds of relatively low molecular weight. Narcosis is seen in acute exposure, but only at concentrations of a few thousand ppm (i.e., more than 0.1% by volume) and hence it is unlikely to occur. Benzene presents a unique and serious hazard. It has been known for some time that it is toxic to the blood-forming components of bone marrow (Gerarde 1960). A review (National Institute for Occupational Safety and Health 1976a) of recent epidemiologic studies compiled substantial new evidence that benzene is a carcinogen with a capacity to cause leukemia in exposed workers. It is now less certain that, as once believed, its myelotoxic effect is immediately arrested on cessation of exposure.

The OSHA standard for benzene is a 10 ppm TWA concentration limit, with a 25-ppm ceiling concentration limit. Because of evidence discussed, NIOSH has recommended (ibid), and OSHA has proposed, a ceiling limit of 1 ppm (3.2 mg/m^3); this is the lowest level at which a reliable measurement is now practical. The OSHA standard for toluene is 200 ppm (NIOSH-recommended standard = 100 ppm); for xylene and styrene it is 100 ppm. Reported bone marrow damage by toluene is believed to be due to benzene impurity (NIOSH 1976a).

Carbon Disulfide--
This is a liquid that boils at 46°C. It induces acute effects in the central nervous system at about 300 ppm and is considered immediately dangerous to life at about 3000 ppm; in the open, these levels would require a large leak from a stream rich in CS_2. Chronic poisoning is a more serious hazard. Effects have been most freqently reported in the central nervous system but there are indications of a range of target organs. A study of workers exposed to carbon disulfide plus about 10% hydrogen sulfide at 10 to 40 ppm showed increased incidences of coronary heart disease and hypertension (Hernberg et al. 1970).

The OSHA standard is a 20 ppm TWA concentration limit, a 30-ppm ceiling limit, and a 100 ppm/30 min limit for a single peak. The NIOSH-recommended standard is a 1-ppm TWA limit, 10 ppm/15 min ceiling limit.

Carbon Monoxide--

This gas is a chemical asphyxiant causing acute symptoms rapidly at 1000 ppm and above and in 1 hour at about 500 ppm. The symptoms are generally those of hypoxia. The intoxication is reversible but hypoxemia sufficient to cause unconsciousness may leave permanent damage. Susceptibility varies considerably, being increased by any condition predisposing to cellular hypoxia, especially of the central nervous system. The hazards of chronic low-level exposure are not to be ignored. In particular there is some indication of cardiovascular effects (U.S. Department of Health, Education and Welfare 1972).

The OSHA standard is a TWA limit of 50 ppm; NIOSH has recommended a 35-ppm time-weighted average limit and a 200-ppm ceiling limit.

Carbonyl Sulfide--

This gas is a slight irritant; it exerts its principal effects on the central nervous system. It is likely to be found in association with carbon disulfide and hydrogen sulfide and it is toxicologically similar to them. There is little evidence about its human toxicity but it probably is less hazardous than hydrogen sulfide. (The inhalation concentration for lethality in mice is much higher.)

There is no occupational standard for this chemical.

Heterocyclic Aromatics--

These are liquids and solids of moderate to high boiling point. N-heterocyclic compounds are the ones of main interest. The one-ring pyridine and its derivatives are generally irritant and narcotic, and hepatorenal injury has been reported. Their significance as hazards in coal gasification is uncertain; it may be as irritant potentiators of carcinogenesis rather than as direct toxicants. The multi-ring N-heterocyclics, and especially the acridines, present a more conspicuous hazard. They are strong irritants of skin and mucous membranes and have a special significance in coal tar as proven agents of irritancy and photosensitization. During estimation of the carcinogenic and other hazards of coal carbonization products, the acridines must be taken into account as potentiators. There also are indications of mutagenic and other effects associated with the O-heterocyclic (e.g., dibenzofuran) and S-heterocyclic (e.g., dibenzothiophene) compounds which are known to occur in coal conversion process streams.

The OSHA standard for pyridine is a TWA limit of 5 ppm; there is no standard for acridine.

Hydrogen Chloride--

This gas is very soluble in water. It is an intense irritant, apparently without irreversible effect at tolerable concentrations.

The OSHA standard is a 5-ppm ceiling limit.

Hydrogen Cyanide--

This is found as a liquid or gas (boiling point 26°C). It acts as a chemical asphyxiant by inhibiting a cellular respiratory enzyme. Possible acute effects include immediate death at 270 ppm and death after 10 minutes at 181 ppm. Exposure at 18 to 36 ppm is said to cause slight symptoms after several hours (Patty 1962). Chronic effects are those of moderate hypoxia, including symptoms such as weakness, vertigo, nausea, rapid pulse, headache, flushing of the face, and gastric distress. Also, skin penetration by the vapor can be dangerous.

The OSHA standard is a 10-ppm TWA limit. The NIOSH-recommended standard is a 5 ppm/10 min ceiling limit.

Hydrogen Sulfide--

This gas is a dangerous acute poison at concentrations of about 400 ppm and up; it therefore calls for emergency protection where such concentrations might occur, such as in the immediate vicinity of H_2S-rich process streams. It affects the nervous system and induces respiratory failure. The warning odor is soon ignored because of olfactory fatigue and collapse may be sudden. Chronic low-level exposure may induce various symptoms of malaise. The gas is a strong irritant of the eye and respiratory tract at about 100 ppm and above, and a slight irritant at 10 ppm. There appears to be no clear evidence of chronic injury from it or of its potentiation of other toxicants. (Methyl mercaptan and other thiols might be encountered. Their toxicology is generally similar to that of hydrogen sulfide.)

The OSHA standard is a 20-ppm ceiling limit, 50 ppm/10 min peak limit. NIOSH has recommended a 10 ppm/10 min ceiling limit and continuous monitoring in areas where a concentration of 50 ppm (70 mg/m^3) may occur, requiring evacuation (NIOSH 1977b).

Mineral Dust or Ash--

Processes such as coal preparation and the discharge of ash from furnaces release particles which, if airborne in sufficient concentration, enter the hazard spectrum in several ways. Silica and limestone dusts may be encountered in the Bi-Gas and CO_2 Acceptor processes and might cause pneumoconiosis. Coal dust presents a similar hazard that may or may not be dependent on a high content of free silica (Casarett and Doull 1975). However, the induction of pneumoconiosis seems unlikely at coal conversion plants. The exposures are of less intensity than those in the occupations where such effects are seen. Doll et al. (1965), for example, reported that pneumoconiosis was not relatable to coal carbonization in their study. Action as an irritant of the lung (fine particles) or skin (coarse particles) and hence as a promoter for carcinogens and other toxic agents is more likely. The aspect calling for most attention is action as a vehicle for toxicants. Polycyclic aromatic hydrocarbons in the air are preferentially carried on smaller particles (National Air Pollution Control Administration 1969); their respiratory potency as carcinogens is enhanced by adsorption on certain materials (e.g., iron oxide: Saffiotti et al. 1964); and other toxicants may be intensified in effect when associated with particles (e.g., sulfur dioxide: Amdur 1957; Amdur and Underhill 1968).

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Nickel Carbonyl--

This is a liquid with a boiling point of 43°C. Metal carbonyls are generally toxic, nickel carbonyl being regarded as the most hazardous. Inhalation of the vapor affects the central nervous system and may induce acute chemical pneumonitis. Brief exposure at 0.15 ppm is reported to induce transient headache (1975 communication to Threshold Limit Committee, ACGIH by Morgan). It has long been considered a carcinogen and the ACGIH recommended a TLV of 0.001 ppm. This view has been challenged however (e.g., Doll et al. 1970) and the 1976 recommended TLV is 0.05 ppm. However, the NIOSH recommendation to OSHA is that it continue to be considered a suspected carcinogen with an exposure limit of 0.001 ppm (1 ppb) (NIOSH 1977c).

The OSHA standard is a TWA of 7 $\mu g/m^3$.

Nitrogen Oxides--

Of these gases, nitrogen dioxide is generally the most conspicuous hazard. It is an irritant of insidious effect because it can penetrate the lung deeply without immediate severe discomfort and induce a delayed pulmonary edema, which may be fatal. However, nitrogen oxides are likely to be produced only if there is high-temperature combustion (steam plant or combustion of wastes) and even then only in low concentrations. A possible, but unproven, hazard is in association with carcinogenesis. There is an indication of lung tumor by nitrogen oxides in susceptible mice. A further possibility is reaction of nitrogen oxides with vapor from glycolamine scrubbers or other amines, forming carcinogenic nitrosamines (see below).

The OSHA standard for nitrogen dioxide is a TWA limit of 5 ppm. NIOSH recommends a 1-ppm ceiling limit.

Nitrosamines--

The simplest members of this group — e.g., dimethylnitrosamine and diethylnitrosamine — are liquids with boiling points in the range of 150° to 200°C and can exist at significant vapor concentrations. They are exceptionally potent carcinogens, and although their presence has not been demonstrated at coal conversion plants, it has been hypothesized that nitrogen oxides from combustion processes might react with vapors from glycolamine scrubbers or with other amines. Dimethylnitrosamine was identified as a mutagen by Legator (1974).

Phenols--

These may be either solids or liquid mixtures of moderate to high boiling point. Phenol and related aromatic hydroxy compounds can be absorbed through the skin and some (e.g., phenol) are sufficiently volatile to be possible respiratory hazards; others (cresols) are less volatile and present an unlikely vapor hazard. Their toxic effect is primarily on the central nervous system and they are also strong irritants. It is the latter property which is likely to be the more significant in coal conversion plants, in the enhancement of carcinogenicity through the presence of phenols in skin contamination by tars or oils or in inhaled particles. Tye and Stemmer (1967) exposed mice to coal tar aerosols by inhalation; with phenols removed, the tar was less carcinogenic.

The OSHA standard is a TWA limit of 5 ppm. NIOSH has recommended a 20 mg/m^3 TWA limit and a 60 mg/m^3/15-min ceiling limit.

Polycyclic Aromatic Hydrocarbons--
Examples are benz[*a*]anthracene, benzo[*a*]pyrene, dibenz[*a*,*h*]anthracene, dibenzo[*b*,*d*,*e*,*f*]chrysene, 3-methylcholanthrene. They are typically solids of high boiling point (of the order of 400°C) and the active members are very well established as skin carcinogens, less so as respiratory carcinogens, and in some cases, clearly implicated as carcinogens at other sites. Benzo[*a*]pyrene (B*a*P) is widely used as an example and as a proxy for the group because it is strongly carcinogenic and very common in circumstances where high-boiling polycyclic aromatic hydrocarbons are found. It is used here as a model.

B*a*P was identified as a specific carcinogen in coal tar by Kennaway (1955). It was already well known as a carcinogen from many animal experiments and there is also some direct evidence to support the extrapolation of this characteristic to man. Human skin treated with repeated daily application of B*a*P in benzene showed changes which were reversible but typical of morphology preceding neoplasia (Cottini and Mazzone 1939). Accidental exposures gave similar indications (International Agency for Research on Cancer 1973).

A normal type of dose-response relationship is clearly seen in mouse skin-painting experiments. For example, the combined results of three experiments in which mice received daily skin applications of B*a*P in acetone were as follows:

Daily dose, μg B*a*P	Day at which 25% of mice were tumorous	Cumulative dose, μg B*a*P
15	122	1830
	105	1875
10	143	1430
	142	1420
5	192	960
	193	965
	235	1175
2.5	281	703
1.25	402	503

Adapted from National Cancer Institute (1977).
These results are also displayed in Figure 18.

A similar dose response relationship was seen in regard to the incidence of lung cancer induced by instillation or implantation of B*a*P — e.g., Laskin et al. (1970) — but nothing comparable was observed for cancer induction by inhalation of B*a*P or of B*a*P on carrier particles.

A positive correlation was obtained between carcinogenicity and mutagenicity of dibenz[*a*,*h*]anthracene metabolized with rat liver homogenate and tested against a Salmonella typhimurium mutant (Teranishi et al. 1975).

OSHA has prescribed no "safe" exposure limits for these proven carcinogens.

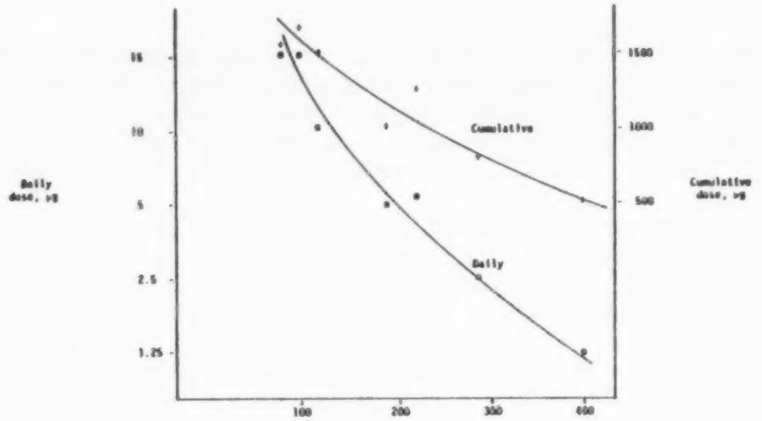


Figure 18. Days at which 25% of mice were tumorous versus daily dose and cumulative dose of BaP (μg).[a]

[a]Adapted from National Cancer Institute (1977).

Sulfur Oxides--

These gases or aerosols may be present in significant amounts if fossil fuels or sulfur-containing wastes are burned at or near the plant. Sulfur dioxide is an irritant, affecting chiefly the upper respiratory tract. Its significance at coal conversion plants is as a possible cocarcinogen (Laskin et al. 1970). This may be due to its irritancy, in which case the sulfuric acid and sulfates which may be found in combustion products or formed by oxidation of sulfur dioxide are also potential hazards, being generally more intense respiratory irritants than SO_2. Their irritancy may be intensified, moreover, by the presence of other particulate matter.

The OSHA standard for sulfur dioxide is a TWA limit of 5 ppm. NIOSH has recommended a 0.5-ppm TWA limit.

Trace Elements--

It does not appear that any trace elements in dust, ash, etc., will be significant hazards in the general atmosphere at gasification plants because of their probably low concentrations, but they require consideration in relation to operations such as the cleaning of filters, quench water ponds, and furnace stacks, and maintenance work in the top of gasifiers, etc. An example of this is quoted later, under "Vanadium." A great difficulty in evaluating hazards is that toxicity is heavily dependent on chemical state and occasionally also on physical state. Elementary analysis is of little value in predicting hazards, which may range from severe in one chemical state to negligible in another. Notes are presented here on some minor constitutents of coal that may be encountered in ash, flue dust, etc.

Arsenic (inorganic)--Effects of chronic exposure include anemia, gastric disturbance, renal symptoms, and ulceration. It is a suspected carcinogen. The OSHA standard is a TWA limit of 500 μg/m^3. NIOSH has recommended a 2 μg/m^3/15-min ceiling limit.

Arsine might be encountered. Chronic exposure to arsine produces effects similar to those of arsenic dusts and fumes. The OSHA standard is a TWA limit of 0.05 ppm.

Beryllium--Overexposure to this metal induces a characteristic syndrome in which respiratory symptoms are conspicuous among others involving the lymphatic system, liver, spleen, and kidney (Eisenbud et al. 1949). Beryllium is a proven carcinogen in animals. The OSHA standard is a TWA limit of 2 μg/m^3, and a 25 mg/m^3/30-min ceiling limit. The NIOSH-recommended standard is the same.

Cadmium--Chronic exposure to cadmium is associated with a variety of effects, among which are emphysema and renal injury (proteinuria). Cadmium has been found in serum samples around the industrial steel complex in Birmingham, Alabama, and the serum cadmium values showed a significant association with cardiovascular disease (Peakcock 1970). It is a suspected carcinogen in animals (NIOSH 1976b). The OSHA standard is a TWA limit of 200 μg/m^3, and a 600 μg/m^3 ceiling limit. The NIOSH-recommended limits are a TWA concentration of 40 μg/m^3 and a 200 μg/m^3/15-min ceiling.

Lead (inorganic)--Characteristic signs of chronic lead poisoning include blue gums, weakness, anemia, neurological symptoms, and gastrointestinal dysfunctions. Urine/blood monitoring is required. The condition has been discussed in detail by Kehoe, e.g., Kehoe 1959; Kehoe 1962. Some lead components are carcinogens in animals. There is evidence of teratogenicity in the hamster (Ferm and Carpenter 1967) but specific evidence in humans has not been found (Scanlon 1975); fetotoxic effects have been observed (Cantarow and Trumper 1944). The OSHA standard is a TWA limit of 200 μg/m^3. The NIOSH-recommended limit is 100 μg/m^3.

Manganese--Chronic exposure induces a wide range of ill effects. Respiratory dysfunction is characteristic and a correlation of industrial manganese exposure with respiratory function was recently shown by Nogawa et al. (1973). Manganese salts have been reported to be mutagenic: e.g., intraperitoneal manganic sulfate caused cytogenic changes in the blood cells of rats (Markaryan et al. 1966). The OSHA standard is a 5 mg/m^3 ceiling limit.

Mercury (inorganic)--Among the more characteristic consequences of chronic exposure to inorganic mercury compounds are tremors, psychic disturbances, renal damage, and cardiovascular disease. Fetal effects have been observed in some instances in humans and animals (Alonso and DeAlvarez 1960; Gale and Ferm 1971). The OSHA standard is a ceiling limit of 100 μg/m^3. The NIOSH-recommended limit is a TWA concentration of 50 μg/m^3.

Selenium--Chronic exposure induces gastrointestinal disturbance, nervous symptoms, liver and spleen damage, and anemia. The characteristic garlicky breath, frequently reported, may not be apparent if tellurium is absent. Selenium is a possible carcinogen. The OSHA standard is a ceiling limit of 200 μg/m^3.

Vanadium--Exposure to vanadium induces acute and chronic respiratory dysfunction and there are several reports that this has occurred in maintenance workers engaged in cleaning fossil fuel plants, e.g., Fear and Tyrer 1958. The OSHA standard for vanadium fume is a ceiling limit of 100 μg/m^3 and for vanadium dust a ceiling limit of 500 μg/m^3. The NIOSH-recommended limit (1977e) for total vanadium is a ceiling limit of 500 μg (V)/m^3; for metallic compounds and alloys, it is a TWA limit of 1 mg (V)/m^3.

Discussion

The purpose of studying toxic effects is to develop and support recommendations for acceptable exposure limits, monitoring procedures, and other protective measures. The usual basis for such recommendations is quantitative expressions of the relation between level of exposure and degree of resultant health effect. These dose-response relationships permit the setting of rational limits for acceptable exposure. This approach will not serve in the present case. A partial solution, recommended in a later chapter, is to use the index that has been adopted for coke oven emissions (Federal Register 1976a), namely, the benzene soluble fraction of total particulate matter (BSFTPM). Use of the coke oven emissions exposure limit also is recommended: 150 μg/m^3 BSFTPM. This has the merit of having been derived from epidemiological evidence but it is to be noted that (1) it assumes similarity between workplace conditions at coke ovens and coal gasification plants and (2) Land's analysis (Federal Register 1976d) did not demonstrate that the coke oven exposure limit provides a safe exposure.

No complete solution to the problem can be seen at present. There are two reasons for this: the complexity of the multifactorial toxic hazard and the uncertainty about safe limits for exposure to carcinogens.

The multifactorial hazard presents a very difficult problem because of the spectrum of possible effects. Respiratory exposure to the range of known toxicants in the coal gasification process streams is potentially carcinogenic in various parts of the respiratory, alimentary, and excretory systems, and toxic to the lung, central nervous system, liver, and bone marrow, to name only the more conspicuous hazards. Furthermore, a number of agents may pose the same threat, a notable example being those polycyclic aromatic hydrocarbons which are carcinogens. If one were dealing with a set of closely similar toxicants, a simple additive effect might be reasonably hypothesized and even validated in animal models, provided that there were dose-response relationships known for each toxicant. We do not in fact have the dose-response data in many cases and we know that the simple additive concept does not apply to many agent interactions. Consequently, it is not possible to estimate quantitative health effects from chemical analysis — even if routine full analysis were practical — or to define an acceptable atmosphere in chemical terms. Nor is it possible to overcome the difficulty of translating chemistry into biology by using a direct biological test, the problems here being the assessment of the long-term effects of chronic low-level exposure and the modeling of multifactorial interactions. Some acute effects might be monitored by whole animal or cellular level exposure, but this is clearly useful only for immediate protective action in a similar way to the canary-in-coal-mine method. Rapid tests for mutagenicity might establish the presence of a carcinogenic hazard but the prospect of their serving as a quantitative model of human response to multiagent exposure is uncertain.

These problems in multifactorial exposure and the controversial issue of safe exposure to carcinogens would seem to dispel any reasonable hope that acceptable exposures can be defined in a manner similar to occupational standards for single toxicants in the near future. It is possible, however, to recommend environmental monitoring, work practices, and protective equipment to minimize exposure.

The greatest toxic hazards in coal conversion are presented by the known and suspected carcinogens, because they are hazardous at low levels of exposure, have delayed action with no immediate warning, and have grave consequences. As for routes of entry, it is to be noted that carcinogenicity is shown by various solids and liquids which may reach the body by inhalation of particles, deposition of particles, or indirectly by contact with dirty surfaces. There are also unproven possibilities of cancer induction by vapor inhalation. Other toxicants are most likely to enter the body by inhalation.

HEAT EFFECTS

Metabolic heat load is determined by conduction and convection currents, radiant heat transfer, and degree of evaporation as well as by the level of worker activity. Responses to increased heat load include cardiovascular strain, fatigue, and depressed psychological performance. If the heat load is excessive or prolonged, frank heat disorders, including heat stroke, exhaustion, and cramps, may occur. It is not expected that heat stress will be a problem in coal gasification plants since most work areas are located out of doors and employees do not have to work in close proximity to the hot reactors. Only during maintenance operations when workers will be required to enter reactors or to repair hot hardware is it expected that problems may occur. Proper work practices and engineering controls are necessary to assure that no undue heat burden is imposed on the employees.

NOISE EFFECTS

The primary adverse health effect of industrial exposure to noise is hearing loss. The pathological event — destruction of the organ of Corti — is clinically manifested as either a temporary or permanent hearing loss, primarily at frequencies above 2000 Hz. Nonauditory noise effects include imbalance and ear pain. High noise levels in coal gasification plants may be found in coal preparation areas, around large compressors, and in utility rooms. Exposures are generally of short duration and are likely to be below the OSHA standard of 90 dba TWA (8 hours).

CONCLUSIONS

1. The overall carcinogenic hazard cannot be precisely estimated from chemical analysis alone, because the possible interactions are far too complex.

2. Further, the hazard cannot at present be quantitatively defined by available biological tests.

3. The same limitations probably apply to toxic effects other than carcinogenesis, with the possible exception of some immediate responses (e.g., chemical asphyxia, primary respiratory irritation).

4. It is not practical to recommend comprehensive workplace exposure limits on a basis similar to those for individual toxicants; however, a limit for one important kind of hazard (high-boiling suspected carcinogens) can be recommended.

5. The carcinogenic hazards associated with airborne particles and surface contamination are the most crucial of the whole spectrum and offer a practical target for control, if not for quantitative evaluation.

6. The only direct quantitative evidence now available is from epidemiology in analogous circumstances and there are severe limitations on the comprehensiveness and reliability of such evidence.

7. Some specific targets for control through industrial hygiene practices can be identified.

8. The presence of any strong irritant of the respiratory mucosa, other mucous surfaces, and the skin should be regarded as a danger signal because of possible potentiation of carcinogens and other toxicants.

EMPLOYEE HEALTH PROTECTION PROGRAM

The purpose of this chapter is to assist existing or future coal gasification pilot plants in developing worker protection strategies that will minimize the potential for acute or chronic illness. Before evaluating what additional controls are necessary, it is desirable to describe the nature of existing pilot plant programs. The current effort is directed almost exclusively toward fire prevention, assurance of safety, and avoidance of gross exposures such as acute carbon monoxide poisoning. This chapter in no way suggests that the effort in these areas be diminished. On the contrary, they are critically important. However, very little attention has been given to evaluating the potential hazards of long-term chronic exposures, particularly those resulting from low airborne concentrations of carcinogenic compounds and coal-derived surface contamination. This sparsity of attention is evidenced by the absence of employee exposure data developed through periodic workplace monitoring.

Without monitoring data to determine the extent and source of potential worker exposures, it is difficult to evaluate program requirements specific to the necessities of each individual pilot plant. Therefore, the recommendations contained in this chapter should be considered a base into which modifications and improvements can be incorporated as the nature of the potential exposures becomes better understood.

Each facet of the employee health protection program is very important to the overall goal of maximizing worker protection. However, because of the nature of the gasification processes and the extent of existing programs, several items deserve special emphasis. The development of effective engineering controls and work practices is imperative now, while the coal gasification industry is still in the pilot stage. If this development is postponed until the industry has proliferated into the commercial stage, the costs in time, dollars, and general effort for retrofit will be an extreme financial burden, and a vastly increased number of workers will be needlessly exposed.

The personal hygiene procedures are critical to the success of the program and should be implemented as soon as possible, without regard to the results of the monitoring program. Efforts to reduce or eliminate skin contamination with coal-derived materials must be coordinated with a comprehensive health education program for all workers.

An effective air sampling program is essential to provide necessary information on potential exposure to airborne toxicants and to set engineering and work practice controls.

ENGINEERING CONTROLS AND WORK PRACTICES

Existing coal gasification pilot plants are essentially closed processes with few continual sources of air or surface contamination. In addition, the processes are frequently down for extensive maintenance and/or system modification during which potential exposure sources are different. Therefore it is convenient to discuss emission sources and suggested engineering controls in terms of the process operating condition (i.e., process down, start-up, onstream operation, and scheduled or emergency shutdown).

Process Down

When the process is down, there are no continual sources of emissions into the workplace; rather, potential exposures will result from maintenance, repair or modification operations that require workers to open process lines or to enter vessels that could contain residual gases or vapors and surface contaminants.

Vessel and Confined Space Entry--

Coal gasification facilities contain large numbers of tanks and vessels (reactor vessels, holding tanks, surge tanks, etc.) of various sizes and geometries. In addition, relatively confined spaces (baghouses, storage bins, and pits) are common. Entry to such areas can pose serious health hazards to employees.

Confined spaces are conveniently defined as any enclosed areas not subject to continuous ventilation or changes in atmosphere by natural air movements adequate to maintain oxygen concentrations at safe levels or to prevent formation of explosive or toxic atmospheres.

Health and safety hazards may arise from several conditions within the vessels or confined spaces:

- Inert atmospheres: Oxygen concentrations well below 19% can be expected to be found in all gasification process vessels. Confined areas such as baghouses may be designed to operate with reduced oxygen levels. Areas where O_2 concentrations are below 19% should be considered hazardous areas.

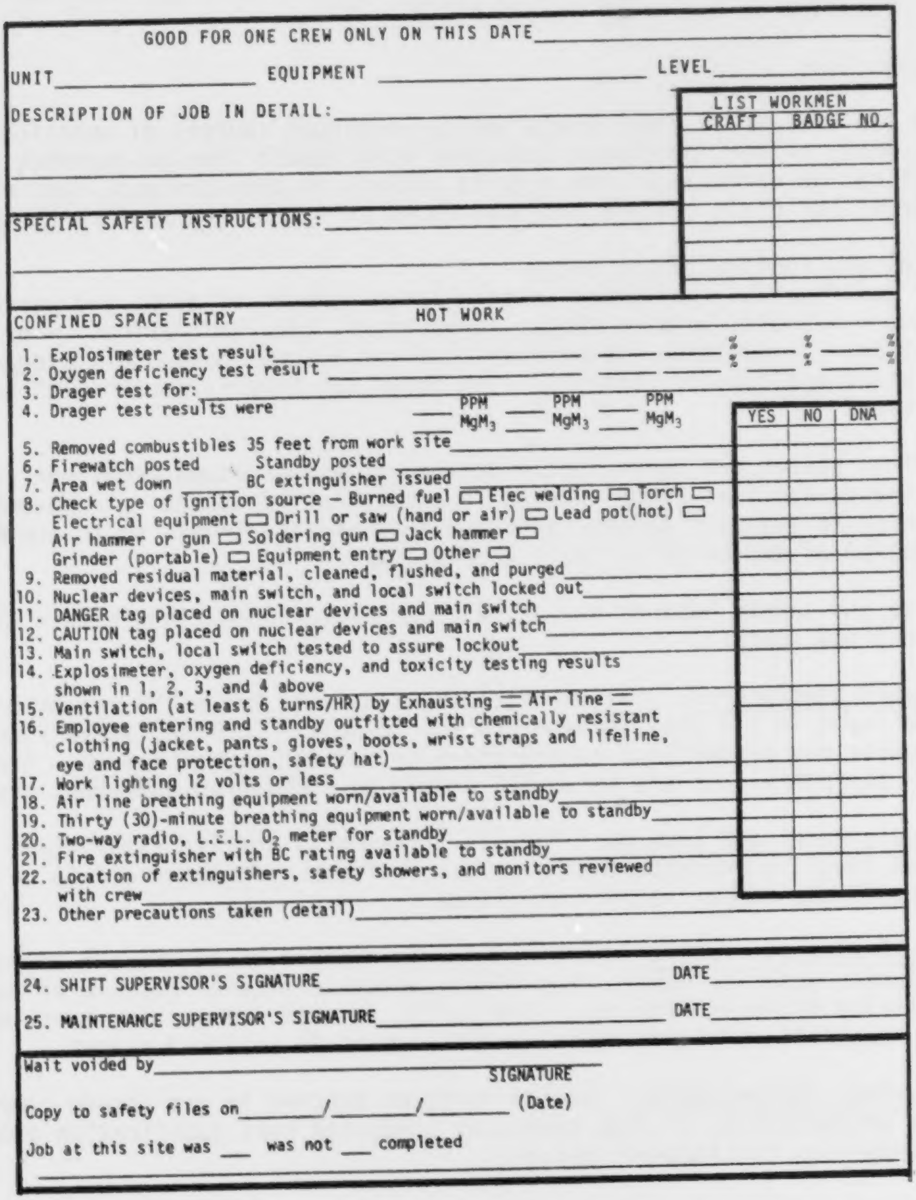
- Toxic gases and liquids: The gas stream will contain a multitude of gas and liquid components that are toxic. These components are to be expected in all gas stream vessels and lines.

- Explosive atmospheres: Enclosed areas exposed to gas stream components may contain gases or vapors from highly volatile liquids capable of forming explosive mixtures with air. Similarly, in coal preparation areas explosive concentrations of coal dust may be present in enclosed spaces.

- Surface contamination: Vessel surfaces exposed to gas stream components will be contaminated, in some cases, by condensed coal gasification products containing carcinogenic material.

The purpose of a safe work permit is to protect the employee from these hazards during normal and emergency situations.

The safe work permit for vessel or confined space entry (Figure 19) is the mechanism by which a "health hazard and work procedure" evaluation is performed for every task requiring personnel to operate in confined areas.



GOOD FOR ONE CREW ONLY ON THIS DATE_______________

UNIT_______________ EQUIPMENT _______________ LEVEL_______________

DESCRIPTION OF JOB IN DETAIL:_______________

LIST WORKMEN	
CRAFT	BADGE NO.

SPECIAL SAFETY INSTRUCTIONS:_______________

CONFINED SPACE ENTRY HOT WORK

YES	NO	DNA

1. Explosimeter test result_______________ _____ _____ % _____ % _____ %
2. Oxygen deficiency test result _______________ _____ _____ % _____ % _____ %
3. Drager test for:_______________
4. Drager test results were _____ PPM _____ PPM _____ PPM _____ MgM3 _____ MgM3 _____ MgM3
5. Removed combustibles 35 feet from work site_______________
6. Firewatch posted Standby posted _______________
7. Area wet down _____ BC extinguisher issued _______________
8. Check type of ignition source – Burned fuel ☐ Elec welding ☐ Torch ☐ Electrical equipment ☐ Drill or saw (hand or air) ☐ Lead pot(hot) ☐ Air hammer or gun ☐ Soldering gun ☐ Jack hammer ☐ Grinder (portable) ☐ Equipment entry ☐ Other ☐
9. Removed residual material, cleaned, flushed, and purged_______________
10. Nuclear devices, main switch, and local switch locked out_______________
11. DANGER tag placed on nuclear devices and main switch_______________
12. CAUTION tag placed on nuclear devices and main switch_______________
13. Main switch, local switch tested to assure lockout_______________
14. Explosimeter, oxygen deficiency, and toxicity testing results shown in 1, 2, 3, and 4 above_______________
15. Ventilation (at least 6 turns/HR) by Exhausting __ Air line __
16. Employee entering and standby outfitted with chemically resistant clothing (jacket, pants, gloves, boots, wrist straps and lifeline, eye and face protection, safety hat)_______________
17. Work lighting 12 volts or less_______________
18. Air line breathing equipment worn/available to standby_______________
19. Thirty (30)-minute breathing equipment worn/available to standby_______________
20. Two-way radio, L.E.L. O_2 meter for standby_______________
21. Fire extinguisher with BC rating available to standby_______________
22. Location of extinguishers, safety showers, and monitors reviewed with crew_______________
23. Other precautions taken (detail)_______________

24. SHIFT SUPERVISOR'S SIGNATURE_______________ DATE_______________

25. MAINTENANCE SUPERVISOR'S SIGNATURE_______________ DATE_______________

Wait voided by_______________ SIGNATURE

Copy to safety files on_____/_____/_____ (Date)

Job at this site was ___ was not ___ completed

Figure 19. Safe work permit (CO_2 Acceptor Pilot Plant).

Vessel and confined space entry procedures can be subdivided into five basic operations.

Preparation of Vessel--Before the vessel is opened, all material must be drained or pumped from it and disposed of or stored in a suitable manner. The vessel should then be flushed with steam or chemical solvents to remove all toxic gases or chemical residues. Next, it should be depressurized, if necessary, and flushed with inert gas. Use of air at this stage may result in formation of explosive air-vapor concentrations if residual amounts of flammable solvents or gas remain in the vessel.

Isolation of Vessel--The vessel should be mechanically isolated from gas stream lines and other sources of hazardous material either by blanking off entering lines with caps or plugs, or by removing a section of pipe.

Other methods such as closing valves and draining do not provide the desirable feature of the positive break between the line and the vessel. The policy of relying totally on valves is to be discouraged.

When unavoidable, shut valves should be chained and double locked by the shift supervisor and workman.

Ventilation--Fresh air should be introduced into the vessel by exhausting the existing vessel atmosphere with ventilation fans and flexible ducts. Exhausted air should not be dumped into areas where ignition sources exist or where personnel may have an opportunity to come into contact with them. Further, the contaminated air should be treated to prevent environmental contamination.

If the vessel has only one opening, a flexible exhaust duct should be extended as far into the vessel as possible and attached to a high-volume exhaust fan. The geometry of the vessel should be considered during ventilation operations to preclude the possibility of leaving dead air spaces, which may contain toxic or explosive gases and vapors.

Testing of Atmosphere--After ventilation and prior to human entry, the atmosphere within the vessel must be checked for the following:

- Presence of adequate oxygen concentration, at least 19%
- Explosive atmospheres (Atmospheres greater than 1/10 of the lower explosive limit should never be exceeded.)
- Presence of toxic gases and vapors, determined by direct reading indicator tubes or instruments

General Safety Procedures--If it is determined by measurement that toxic gases or vapors are present or that adequate oxygen concentrations cannot be maintained within the vessel or confined area, then respiratory protective equipment must be provided as described in later sections on respiratory protective equipment.

A "buddy system" must be used whenever personnel are required to enter vessels or other confined spaces. The standby employee should:

- assist in moving tools or equipment,
- keep in continuous contact with the person inside the vessel, and
- initiate rescue of person in the vessel if required.

No more than one employee shall enter any one vessel unless means are available to retrieve all personnel in an emergency.

Process Line Opening--
Frequently it is necessary to open process lines to remove or change equipment such as pipes or compressors. Depending on where these lines are in the process, they may contain residual gases, vapors, and/or liquids. As with vessel entry, a safe work permit requiring a comprehensive safety and health hazard evaluation should be completed prior to these operations. As a minimum precaution, a double block and bleed valve arrangement (Figure 20) should be available and used. The line should be blocked upstream and downstream of the two flanges or joints prior to opening the bleed valve.

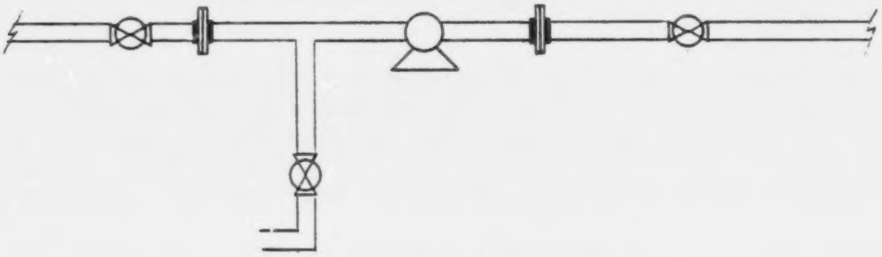


Figure 20. Pump and shut-off valve.

Unfortunately, a potential health hazard may be caused by emissions from the bleed line. If the health hazard evaluation indicates that toxic material may be emitted, a portable or permanent exhaust hood should be used to remove any toxic gases or vapors to the flare. The bleed valve should be gradually opened over a period of time to prevent high-velocity discharges under pressure, which could negate the benefit of the exhaust hood. Obviously, if liquids are anticipated, the bleed line should be connected to a container to prevent work surface contamination.

A formal, well-scheduled preventive maintenance program can be very useful in reducing the frequency of leaks during process operations. Primary targets for frequent examination include pump and compressor seals, valves, and gaskets in flanges and vessel hatches. Scheduled replacements, regardless of need, should be considered in attempts to eliminate problems before they have a chance to occur. The scheduled changes should be planned to coincide with process down time.

Process Start-up

Start-up procedures vary from plant to plant, but it is important that each include a thorough leak testing sequence using inert gases in the system.

Clearly, if leaks can be located and corrected before the process is started, sources of potential health hazards will be reduced, as will the probability of emergency shutdowns.

Before the inert gases are brought into the system it is beneficial to tape the perimeters of all flanges with duct tape. The tape will turn brown if the flange is leaking and thus the search for leaks is simplified.

To initiate the testing sequence, all valves within a given section should be opened, the compressors started, and the inert gases admitted and gradually pressurized to operating pressure. Each section should then be held at pressure to determine whether there is either a pressure drop within the section or a detectable leak. Once cold leak testing is completed, the pressure may then be reduced and heat-up may be started. At 50% of operating temperature, leak testing may be repeated, and it should include inspection of taped flanges.

Because there are many potential sources of leaks, as many as possible employees should assist in the search. An adequate number of portable gas detectors is also necessary. All leaks must be corrected by tightening flanges, changing gaskets or seals, or replacing nonrepairable equipment (Oral communication, February 14, 1977, by K. Martin, 6205-101 Avenue, Apartment 707, Edmonton, Alberta, Canada).

Onstream Operation

When the process is under normal operating conditions, there should be very few if any continuous sources of workplace emissions or airborne toxicants. All of the processes are essentially closed, and most operate under such high pressures that continuous leaks could not be tolerated without a severe fire hazard or an adverse effect on essential operating parameters. Low-pressure processes may require extra precautions because leaks could go unnoticed without affecting quality parameters.

Worker exposure can and will occur because of minor leaks, primarily through pump and compressor seals, valves, flanges, and other similar equipment. Thus the most effective engineering control technique should incorporate good process design characteristics and modification conducive to leak minimization; equipment (such as pumps, compressors, and valves) capable of withstanding the severe process stresses induced by high temperatures and pressures and by the existence of slurries in many process streams; and proper seal and gasket materials and design, modification, or equipment selection or development. These are primary goals of the overall coal gasification pilot plant program. Obviously problems associated with each process will have to be solved prior to the construction of full-scale commercial plants.

The question of most effective seals for pumps and compressors does deserve attention because of its importance to leak prevention. Double or even triple mechanical seals (or their equivalent) should be used whenever possible on lines containing toxic materials, because of their effectiveness in preventing leakage. Additional methods of leak reduction are the following:

- The maximum use of welded joints and connections rather than gasketed flanges: The additional burden created by the required welding and cutting should be more than offset by the elimination of leak sources and the reduction in the number of emergency shutdowns.

- The use of local exhaust ventilation in areas of frequent sources of leaks, especially those in enclosed areas: This method has merit where all other control techniques have not been completely effective.

- The development and use of standard operating procedures: The interactions between the workers and the process are critical to preventing upset conditions and the resulting exposures. When a worker makes an error there is a potential for large emissions of toxicants and gross work surface contamination. Although there is little that can be considered standard under pilot plant conditions, employees should be well trained and intimately familiar with proper operating procedures. Written standard operating procedures in conjunction with a formal training program are essential.

However, since the primary control strategy (a tight process) is still in the developmental stage at the pilot plants, a total prevention of leaks is doubtful. Therefore, methods of containing or correcting leaks as they occur are necessary (leak detection strategies are presented in the monitoring chapter and discussed further in this chapter under the heading "Air Sampling Program"):

- For lines containing toxic materials, valves might be "spared" (parallel duplication) so that leaks can be bypassed. A system of parallel pumps and compressors in critical areas is also desirable to bypass leaks without causing an unplanned shutdown.

- A system of long, strategically located flexible exhaust ducts connected to a common main may be practical and effective, particularly in enclosed plant areas. When a leak is located, the flexible duct is positioned to capture and remove the toxicants before they can contaminate the workplace. This type of system eliminates the need for a separate exhaust for each potential leak source, and does not require unusually large volumes of air because the branches can be "deadheaded" or dampered when there are no leaks to contain. The polyvinyl chloride industry uses this control technique extensively and effectively to remove inadvertent leaks of vinyl chloride monomer. To overcome the problem of capturing high-velocity leaks, a low-volume, high-velocity exhaust system should be considered. This type of exhaust system induces extremely high capture velocities.

- For liquid leaks, portable barricades or shields should be considered, to contain and localize the area of surface contamination.

- Drip pans or equivalent containers should be installed under process equipment that has a potential for leaking liquids.

Planned or Emergency Shutdowns

During a shutdown (particularly for processes using a preheater or pretreater) it is desirable to burn off all line material by bypassing it through the gasifier, then to the thermal oxidizer. Following this, the system should be purged repeatedly with inert gases until the process gas chromatographs reflect that the lines are free of gases and vapors. Essentially, this procedure is appropriate for both planned and emergency shutdowns.

In most cases prior to an emergency or involuntary shutdown, a concerted effort will be made to remedy the cause of the problem, such as a blocked line. It is conceivable that certain of these efforts may greatly increase the potential for employee exposure to process stream gases, vapors, or liquids. The decision of when the shutdown is necessary must take into account potential health hazards. Although it is important that emergency shutdowns be minimized, worker protection must be the primary concern.

Other Suggestions

- The composition of vented material and location of all process outlet vents should be determined. Preferably, the vents should be fed to the thermal oxidizer, but if not, the outlets should be located such that vented gases and vapors cannot reenter the workplace.

- Enclosed process areas should have adequate general exhaust ventilation and tempered makeup air. Without a continual turnover of air, concentrations of airborne toxicants can build up and cause severe problems.

- The collection of process samples, particularly through the use of "shot pots," can be a source of workplace emissions. Many times there are problems with closing valves, and toxicants can escape over a significant period of time. Consideration should be given to providing local exhaust for these operations. (See chapter on safety.)

- Mixers, separators, and other vessels containing volatile liquids or liquids containing dissolved toxic gases should not be open to the workplace environment.

- The control rooms and lunch facility should be kept under positive pressure relative to the workplace. This may be accomplished using an air supply cleaned through a high-efficiency particulate (HEPA) filter. To encourage maximum use of the facilities and to assist in keeping the doors shut, the supply air should be cooled during hot weather and heated during cold weather.

- The importance of good housekeeping procedures cannot be overemphasized, particularly as it relates to good personal hygiene. Adequate time must be allocated during every shift to clean up and, where necessary, to decontaminate work surfaces. Otherwise, residue will accumulate and greatly complicate the problem. It must be understood that generally workers will not initiate cleanup activities on their own unless convinced of their value — it is not the most pleasant of jobs. The stimulus must come from top management, through the supervisory levels, to the workers. The policy on good housekeeping should be quite clear. Good housekeeping also has a beneficial effect on individual attention to safety, observance of rules, and personal hygiene. It engenders a good frame of mind, which is critical to the success of the overall program.

SUGGESTED INDUSTRIAL HYGIENE PROCEDURES

Health Education Program

Most occupational physicians and industrial hygienists agree that workers must be familiar with the hazards to which they may be exposed. As Eckhardt (1960) aptly stated, "It seems axiomatic that if a man is to protect himself from a hazard he must be informed of the nature of the hazard from which he is protecting himself." This has particular significance for hazards involving skin contact with carcinogenic compounds, where good personal hygiene is essential. It follows that workers should be knowledgeable about the provisions that are available to them for protection against the hazards. They must be educated in the proper use and reason for each protective device or procedure in the program.

A meeting of all employees should be held to describe in detail all potential health hazards, as well as the features of the medical surveillance program. Although exposures to carcinogenic materials will necessarily get the greatest attention, exposure to other potential toxicants or irritants such as CO, H_2S, and coal dust, as well as harmful physical stresses such as noise and heat, should also be discussed. Good preventive health procedures should be stressed.

Existing or newly implemented protective measures should be fully described. Of course, during this meeting there is insufficient time to actually instruct the workers on the specific aspects of the preventive program. This should be done during subsequent meetings and should be a supervisory responsibility. However, each item should be touched on, and the joint responsibility of supervisors and employees in the implementation of this program should be stressed.

To yield any degree of success, the program must be continual, with periodic meetings and continuous emphasis from those in charge.

Topics of discussion during the periodic meetings may include:

- specific operations resulting in high exposures to toxicants, with emphasis on airborne particulate and surface contamination containing carcinogenic compounds and vapors;
- purpose and results to date of the air sampling and work surface inspection programs;
- purpose and proper use of respiratory protective equipment;
- open discussion concerning the protective clothing program;
- purpose and discussion of the work surface cleanup and decontamination program;
- open discussion of improved work practices and engineering control options;
- outline of emergency procedures, including first aid; and
- other topics of importance based on program results to date.

The success or failure of this program hinges on the diligence and support of three groups: (1) plant management, (2) supervisory personnel, and (3) the unions or plant operators.

Personal Hygiene Practices

A strict personal hygiene program is essential for proper worker protection in coal gasification pilot plants. Even if all external sources of skin contamination could be eliminated by extensive engineering and work practice controls, exposures would remain because of frequent operating changes and the concomitant potential for contact with contaminated surfaces inside of process equipment.

Protective Clothing--

The selection of the optimum type and combination of protective clothing is a difficult one requiring trade-offs among several options. The clothing should minimize exposed skin surfaces, provide good repellency against liquids, reduce the passage of vapors and aerosols, and be relatively acceptable to the workers. A rubberized fabric has excellent repellency and is very impervious, but could cause an unacceptable risk of heat stress problems. Many close-knit synthetic fabrics have very desirable protective properties, but they also could cause heat stress problems and they tend to melt when a flame is applied to them.

It is suggested that jumpsuit-type, cotton coveralls will provide a great deal of protection, provided that they are a fairly close weave and are designed not to "breathe" heavily with normal body movements. The coveralls should be white so that contaminated areas will not be masked.

There is evidence that the type of underclothing is very important to the reduction of skin contamination. From an experiment undertaken in 1957 at a coal hydrogenation pilot plant it was concluded that pajamas, buttoned at the neck, with close-fitting arm and leg cuffs, worn under typical work clothes, were very effective (Ketcham and Norton 1960). Apparently this prevents contaminants absorbed into the outer clothing from continually contacting exposed skin beneath it. It also provides an additional barrier to the passage of vapors and aerosols. Regardless of whether normal work clothes or loose underclothes are selected to wear under the coveralls, they should be long sleeved, buttoned to the neck, and have close-fitting arm and leg cuffs.

Gloves are usually worn at coal gasification plants during cold weather, when heavy equipment is handled,or in areas where process equipment is hot. Where gloves will not cause a significant safety hazard, they should be worn to assist in preventing hand contact with coal-derived materials. Gloves also have the secondary effect of reducing the spreading of contaminants from the hand to other parts of the body, particularly the head and face. However, gloves made out of absorbent materials should not be used because, once contaminated, they will remain a constant source of hand contamination until laundered. The preferred glove should be impervious to the absorption or passage of process residue, and capable of withstanding daily laundering.

There should not be large quantities of liquid residue from the gasification process, so work boots should provide adequate protection. However, if problems with foot contamination develop, loose impervious overshoes should be considered. Rubber overshoes are not recommended because of swelling problems caused by contact with process oils.

It would be prudent to conduct tests with several types of clothing and fabrics prior to selecting and purchasing a large number of any one type. The tests should be performed on a small number of employees within a similar job category (preferably those with the highest risk of skin contamination), and a decision based on fluorescence testing of inside fabric surfaces should be made.

Laundering--

Several sources indicate that the best method of ridding work clothes of coal-derived contamination is dry cleaning, followed by washing with soap and water or a commercial detergent (Sexton 1960b). The fact that work clothes should be periodically cleaned is not open to much question, although the proper frequency is. Eckhardt (1960) suggests that if a choice is necessary, a daily supply of clean underclothing is preferable to daily cleaned outer clothing. He states that "(i)n our view, if the clothing in contact with the skin is cleaned daily, the cleanliness of the outer clothing is less important. In our experience at Esso and from studies done by Venable and Wilkening (1958), not enough material is retained by the outer clothing to penetrate clean underclothing for more than the day of contamination, but once contaminated thoroughly, underclothing can repeatedly soil the skin." (It is inferred that outer clothing means anything that is not in direct contact with the exposed skin, i.e., coveralls.) This implies that although the underclothing should be cleaned daily, this frequency is not necessary for the outer clothing.

It is felt that this is unacceptable because of the potential carcinogenicity of the coal-derived residues, the higher possibility of preventable skin contamination for several shifts after the outer clothing is soiled, and the fact that the additional burden of daily cleaning of the coveralls is relatively insignificant.

Because of the large amount of required laundering, it is preferable for each pilot plant to have cleaning facilities. However, whether the cleaning is done in house or commercially, laundry employees should be warned of the hazard of making skin contact with contaminated clothing or laundry fluids.

It is recommended that clean outer garments and underclothing (including socks) be issued to all workers at the beginning of each shift. The effectiveness of the cleaning method should be periodically evaluated by examining laundered clothing under an ultraviolet lamp.

The above discussions place significant responsibility on pilot plant personnel to determine the most effective protective clothing and cleaning programs. This is necessary because specific suggestions could preclude the location or development of better methods, and not enough is known at this point to substantiate specifics.

Further, the discussion implies that it is necessary for all employees who enter the plant processing area to follow the same guidelines. If the personal hygiene program is to be accepted by the workers, it must be administered and adhered to uniformly, with no exceptions. If engineers and other office personnel or visitors enter areas where coal-derived contamination is possible, it is logical to assume that they need equivalent protection.

Locker and Shower Facilities--

In the coke oven industry, showering at the end of each work shift has been cited as one of the most significant factors in preventing skin cancer

(Federal Register 1976a). At coal gasification pilot plants, it is similarly important that employees shower at the end of each shift to assure that skin contamination is removed. Adequate time and well-designed facilities are necessary to encourage adherence to this requirement.

To promote good personal hygiene practices, encourage adherence to the daily shower requirement, and segregate contaminated clothing from street clothing, a double locker room separated by a large shower facility should be installed. The essential features of the double locker room are depicted in Figure 21 and summarized below:

- Two sets of lockers are provided on the clean side for each employee — one set is for street clothing, the other for clean work clothes provided daily.

- A set of lockers is necessary on the contaminated side to allow storage of work boots, hard hats, and other safety equipment. These items are accessible through a one-way door in the partition separating the clean and contaminated sections of the facility.

- Soiled clothing removed following shift activity should be segregated so that outer garments are not mixed with employee clothing in direct contact with the skin. The indiscriminate collection of all clothing may cause the spreading of contamination from overalls, for example, to undergarments.

- Grossly contaminated clothing should be totally segregated from all other clothing for disposal.

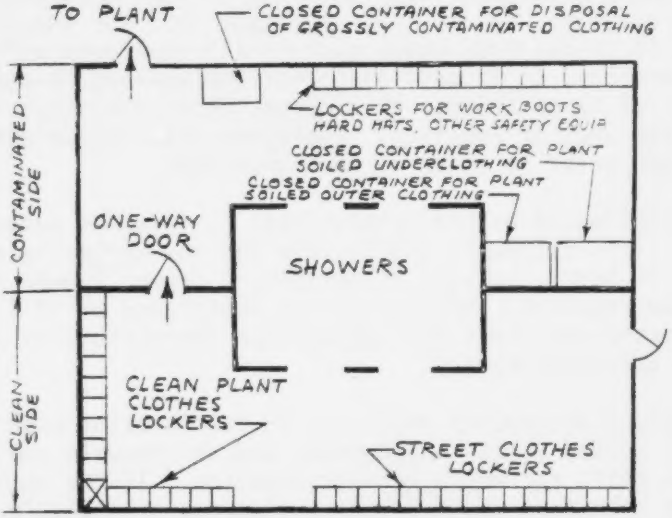

TO PLANT
CLOSED CONTAINER FOR DISPOSAL OF GROSSLY CONTAMINATED CLOTHING
LOCKERS FOR WORK BOOTS HARD HATS, OTHER SAFETY EQUIP
CLOSED CONTAINER FOR PLANT SOILED UNDERCLOTHING
CLOSED CONTAINER FOR PLANT SOILED OUTER CLOTHING
CONTAMINATED SIDE
ONE-WAY DOOR
SHOWERS
CLEAN SIDE
CLEAN PLANT CLOTHES LOCKERS
STREET CLOTHES LOCKERS

Figure 21. Double locker room.

Regular soap is recommended for the shower facility: the use of solvents may transport the contaminants into the skin (oral communication, January 1977, by J. Hultz, Pittsburgh Energy Research Center, 4800 Forbes Avenue, Pittsburgh, Pennsylvania 15213) and thus hinder removal. It is important also that workers thoroughly wash their hair during showers.

General--

After study at a coal hydrogenation plant, Ketcham and Norton (1960) concluded that "(t)he waterless hand soaps appear by far the best." Lanolin based or equivalent nonaqueous hand cleansers should be provided in all washrooms in the plant and in the locker facility. All trips to sanitary facilities should be preceded by a thorough cleansing of the hands.

Barrier creams are frequently mentioned as being of value in occupations where skin contamination or dermatitis is a recognized problem, although actual benefit has not been proven and is a subject of some controversy. It is therefore not possible to fully encourage or discourage the use of barrier creams; at best, they may only be considered a minor adjunct to the overall protective program. Unless the efficacy of specific barrier creams can be proven, workers should not be required to use them. However, the creams should be made available to employees for use upon request or under advisement of an occupational physician.

The presence or consumption of food, beverages, and smoking material, and the application of cosmetics, should be restricted to designated areas that are enclosed, under pressure from a clean air supply, and not contaminated with process residues. It is preferable to have a central lunchroom for this purpose, but control rooms or other areas that meet the above requirements are acceptable.

An adequate number of washrooms should be provided throughout the plant area to encourage frequent cleaning by workers. In particular, a washroom facility is necessary in close proximity to the lunchroom so that employees can wash thoroughly prior to entering. It is very important that the lunchroom remain uncontaminated as it is one area where most or all employees will consistently congregate. Therefore, it is advisable that the workers remove their gloves and hard hats prior to entering. This necessitates the provision of some type of interim storage area or facility. Employees with contaminated coveralls should change them prior to entering the lunchroom.

If gross contamination of either exposed skin surfaces or outer clothing occurs during a shift, it is extremely undesirable for the worker to remain exposed until the shift is over. In such situations, a prompt shower and change of clothes should be required. Because of the importance of this protective measure, supervisory employees must accept the responsibility of assuring strict compliance with this requirement.

The personal hygiene procedures described in this section must be supplemented with a continual worker education program, and an adequate amount of time should be allotted each shift for employee participation. If the necessary time and training are not provided, the protective programs will simply not be effective.

Respiratory Protection

Respirators are considered a "last resort" method of reducing employee exposure to airborne toxicants, acceptable only after it is demonstrated that engineering, work practice, and/or administrative controls are not sufficient, during the interim period until effective controls are implemented, or in hazardous operations or emergencies. The primary goal of the health protection program should be the control of process emissions at the source to eliminate employee exposure and the resulting need for respirators. The source control strategy is important because respirator use may not afford adequate protection. For example, the fit may be poor, or the respirator may not be used because of worker discomfort or ignorance about the fact that a significant airborne exposure exists. Further, respirators interfere with communication, may contribute to heat stress problems, frequently cause facial rashes, and if not maintained properly, will not provide protection even when worn.

However, during certain maintenance operations (these are frequent in pilot plants), during leak conditions, and while effective controls are being developed, respirators are necessary. Since it is apparent that they will be needed periodically, an evaluation of the proper respirator is necessary. The selection of respirators is dependent upon the following:

- The airborne toxicants causing the potential health hazard, its hygienic standards, and its olfactory warning properties
- The physical state of the airborne toxicant (i.e., gas, vapor, aerosol)
- The estimated maximum concentration of the toxicant in relation to its hygienic standard
- The job requirements of the workers (e.g., mobility around moving equipment)

Potential airborne toxicants in most pilot plant areas include a large and complex variety of gases, vapors, and aerosols. Of the currently available respirators, only a supplied air system can provide protection against the wide range of anticipated exposures. Unfortunately, supplied air respirators require umbilicals in the form of air lines or hoses, which reduce mobility, introduce unacceptable additional safety hazards, and may restrict immediate escape during an emergency. Although supplied air respirators have been successfully integrated into other segments of the chemical industry without overwhelming problems, a coal gasification pilot plant is unique because of the frequent process changes, continual maintenance requirements, and peculiar safety hazards associated with the extremely high operating temperatures and pressures. Except at very restricted maintenance operations where the oxygen may be deficient, where large concentrations of gases (CO, H_2S) may be anticipated, or during emergency conditions, supplied air respirators are not suggested. However, self-contained air or air line respirators should be readily available at all times for use when needed.

Until a respirator is developed that can provide protection against the wide range of toxicants emitted during coal gasification process leaks, specific toxicants must be selected as the basis for respirator determination. A precedent exists in the coke oven industry, in that a similarly wide range of airborne toxicants is emitted into the workplace. The coke oven emissions standard (Federal Register 1976a) recommends protection against carcinogenic particulate matter and specifies respirators accordingly, based on the airborne concentration of coke oven emissions. For concentrations not greater than 1500 $\mu g/m^3$ benzene soluble compounds (as the benzene soluble fraction of total particulate matter), the recommended respirator provides protection against organic vapors and particulate matter. In coal gasification pilot plants, a combination particulate matter and chemical cartridge respirator is suggested for maintenance and operating personnel for protection against carcinogenic aerosols and organic vapors such as benzene. A formal respirator program that meets the requirements of Title 29 CFR 1910.134 should be mandatory.

This respirator should be carried by every employee while in operating areas, and is recommended for use except in the following circumstances:

- During emergency conditions when an employee has to be in the immediate area of a bad process leak: In this situation, high concentrations of toxic gases (CO, H_2S) could be anticipated and could cause acutely adverse effects. Supplied air respirators are necessary for this type of emergency condition.
- During vessel entry when tests have shown that the oxygen is deficient (<19%), that CO concentration >35 ppm, or that H_2S >10 ppm: Further purging and ventilation are necessary prior to entry.
- In areas where carcinogenic particulate matter or organic vapors are not the prime concern, for example, in the acid gas cleaning process where H_2S is of primary concern, or around certain methanators, where nickel carbonyl may contaminate the workplace: In these instances, respirators designed specifically for protection against the particular toxicants are required.

Regulated Areas

There are several reasons for designating and posting regulated areas, including the following:

- Restricting employee entry into the area
- Specifying the required type of personal protective equipment and controlling usage
- Pinpointing employees in the area who should have additional protective requirements

All occupational health standards to date have relied heavily on the concept of regulated areas to simplify the task of administering and regulating the requirements of the standard. When one toxic agent or one area (e.g., coke ovens) is concerned, the determination of which areas should be regulated is a straightforward and relatively simple task. Employees remain in essentially the same area; emissions are relatively constant; and periodic personal monitoring can provide a very good estimate of worker exposure. Unfortunately, this is not the case in coal gasification pilot plants, where there are multiple toxicants potentially entering the workplace from various sources and at different times. To complicate the matter further, the various process areas are usually in close proximity to each other and not enclosed, so leaks of toxicants in one area may contaminate work areas throughout the plant. Further, employees frequently move throughout the plant area, experiencing numerous potential exposures from many different sources. The typical regulated area concept is thus not totally applicable to coal gasification pilot plant conditions.

Several options may accomplish the purposes derived from the usual regulated area concept:

- Job functions are regulated instead of work areas. All jobs that involve opening or entering any process vessel, line, or other piece of equipment should be considered regulated. Most maintenance jobs and tasks such as sample taking will fall into this category.
- Process areas are regulated if the results of the monitoring program show that the concentration of any of the following routinely exceeds the indicated limit:

  Carbon monoxide (35 ppm)

  Hydrogen sulfide (5 ppm)

  Benzene solubles (150 $\mu g/m^3$ in any area other than coal storage and preparation)

  Respirable particulates (2.0 mg/m^3 in the coal storage and preparation areas)

  Benzene (1 ppm)

  This will apply primarily to enclosed plant areas; open plant areas may exceed the indicated levels during a leak condition but the frequency should be low.
- Plant areas with work surfaces that are frequently contaminated with coal-derived materials should also be regulated. The same is true for plant areas where gross contamination has occurred. Entry into these areas should be restricted to the extent that no employee should risk potential skin contamination unless entry into the area is absolutely necessary.

Everyone who enters these areas should be required to wear respiratory protective devices until engineering controls can be installed to reduce exposure to acceptable levels. Entry into the regulated areas must be strictly on a need basis.

Posting

Posting warning signs at various plant areas reinforces adherence to the requirements of the overall health protection program. The signs serve as periodic reminders to workers that potential hazards exist and protective measures are necessary. To be effective the signs must be kept clean and visible, and should be illuminated at night.

Because work surfaces in many plant areas may be contaminated with coal-derived compounds, all entrances to plant process areas should be posted. Example:

CAUTION

Work Surfaces
May Be Contaminated
With Cancer Suspect Agents

Authorized Employees Only

Protective Clothing Required

Avoid Contact With
Process Liquids or Residues

Smoking and Eating Restricted
to Designated Areas

Although it may be argued that these signs should be selectively posted only in areas of known harmful contamination, it is important that workers consider all surface contamination potentially hazardous.

Entrance to regulated areas should also be posted. Example:

CAUTION

Cancer Suspect Agents*

Respiratory Protection Required

Authorized Employees Only

During regulated job functions (e.g., maintenance work), the work area should be cordoned off and a warning should be posted at the extrance. Example:

CAUTION

Restricted Area

Authorized Employees Only

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*Because of the number of possible toxicants, this general statement is suggested. In regulated areas where carcinogens are *definitely* not present, different or more specific statements are preferred (e.g., "Dust Hazard," "Hydrogen Sulfide Present," "Toxic Gases and Vapors Present").

Labeling

In the developing stages of fluid catalytic cracking in the petroleum industry, an integral part of the control program was the identification, labeling, and painting of all tanks, lines, or other equipment that might contain carcinogenic oils. In addition, process samples and contaminated equipment going to repair shops were identified with brightly colored tags (Holt et al. 1951). This helped to warn employees that a potential hazard existed, particularly during maintenance operations or when a leak occurred. A similar approach is of value for coal gasification pilot plants. All process equipment containing carcinogenic compounds should be identified by a brightly colored paint. Process vessels should be painted and labeled. Example:

CAUTION

Contains Toxic Materials

Equipment or other items that are contaminated with coal-derived materials should also be identified with a brightly colored tag.

Surface Cleanup and Decontamination

There are three types of cleanup and decontamination problems.

Liquid Spills or Leaks--

Once a significant leak or spill is located, it must be contained as quickly as possible to minimize the area of contamination. Extreme care must be exercised by workers involved in the cleanup to reduce the potential of gross skin contamination. The first step in the containment of the spill is to locate the source of the spill or leak and correct the problem. This correction may be as simple as tightening a pump seal packing gland or switching to a "spared" valve, or as drastic as initiating a process shutdown. Next it is necessary to contain the spread of the contamination by perimeter diking, using heavy work cloths, or materials such as long lengths of lumber. After the spill is contained, several methods can be employed to transfer the liquid into sealed, impervious containers. Squeegees and scoops can get up the bulk of the liquid, and then absorbent particles can be deposited and swept up when the remaining liquid is absorbed. Alternatively, portable suction pumps can be used to transfer liquids into a container for disposal. Finally, it is necessary to clean the surface with commercial detergents and a stiff brush. Water flushing should not be used to disperse and remove liquid spills, however minor, because the area of contamination may be increased.

Other Surface Contamination--

Dried, condensed tars are difficult to remove from any surfaces and particularly from the inside of process vessels. Manual scraping and chipping of the surfaces, coupled with the use of chlorinated hydrocarbon solvents or commercial cleansers, are frequent methods of cleanup. Where solvents are used, special care is necessary to prevent more hazardous exposures to solvent vapors. Cleaning solvent should be selected in terms of low toxicity and vapor pressure, and respirators should be worn. Steam stripping is also used extensively and is effective, but it should be noted that severe airborne exposures to potential carcinogens may result. Lower boiling point residue may vaporize and high boiling point material may become entrained in induced air currents. Generally, steam stripping is not recommended because of this potential for gross air contamination, but there may be instances (e.g., small, confined surfaces) where it is essential. It is recommended that if steam stripping is used, supplied air respirators be worn by all employees.

Tools and Equipment--
Hand tools and portable equipment may frequently become contaminated with coal-derived materials and present an exposure to employees using them. These should be periodically cleaned with detergents and/or solvents. Again, care must be taken to prevent exposure to hazardous solvent vapors. Before the tools or equipment are returned to service they should be examined for residual contamination in an ultraviolet dark box.

A UV scan of the affected areas following decontamination will determine whether additional cleaning is necessary. All employees involved in the cleanup operation should be required to shower and change clothes after the operation is completed.

Soiled work clothes and other materials used during the cleanup must be placed in closed containers for disposal. Reusable items such as scraping or chipping tools should be placed in closed containers for transfer to specially designed areas with adequate ventilation for cleaning and decontamination.

Record Keeping

In a new industry where no useful precedents exist and there are more questions than answers, it is imperative that complete records be developed and maintained. Pilot plant personnel would not think of completing a process without recording and maintaining all pertinent data on operational parameters and results. These data are critical to the performance of future runs and imperative for the determination of the nature of future demonstration and commercial plants. It is similarly essential that thorough records of all aspects of the health protection program be produced and maintained.

Detailed records of the following activities should be maintained:

- Air sampling: Date, instrumentation, and analytical method; location if area sample; employee name and job classification if personal sample; operating conditions, and meteorological conditions (if outdoors), during the sample; duration of sample; sample air volume; sample result; additional information as required to evaluate employee exposure or for other purposes such as prospective epidemiology studies.

- Leak detection: Date, instrumentation; location, concentration, and cause of the leaks; method of containment or repair (it is beneficial to categorize leak data to assist in analyzing trends or diagnosing problem areas for investigation — for instance, frequent leaks from a particular valve or flange).

- Training: Date, employee group, type of training or meeting, objectives, significant results.

- Preventive maintenance: Equipment, location, scheduled date, completion date, outcome.

- Medical records: See chapter on medical monitoring.

AIR SAMPLING STRATEGY

The measurement and subsequent evaluation of workplace concentrations of airborne toxicants are fundamental to an effective and efficiently administered health protection program. It is absolutely necessary for pilot plant personnel to initiate a monitoring program designed to yield pertinent and timely data on the nature, sources, and extent of the existing exposure.

The suggested features of the sampling programs are discussed in the following chapter, "Monitoring the Worker's Environment," and consist of the following:

- Quick response monitoring for selected indicator gases such as CO or H_2S

- Personal monitoring for benzene soluble compounds, measured as the benzene soluble fraction of total particulate matter (BSFTPM)

- Workplace area monitoring and the evaluation of worker exposure in all enclosed areas conducted in accordance with existing standards.

Monitoring for the selected indicator gases is the foundation of the sampling program, and thus, it must be continually emphasized. In pilot plants where the gasifier section is enclosed, a permanently affixed, multiple gas monitoring system is recommended. If there is a leak, CO or H_2S concentrations will build up until one of the sampling heads picks up a high reading. At this point, a system of warning lights should be activated, and two actions are required:

- The workers in the areas will have to put on respirators until the warning lights go out, indicating that the potential hazard has subsided.

- A designated worker will immediately use a portable gas analyzer for a systematic search to locate the source of the exposure. Once located, the leak may be repaired on the spot, contained by local exhaust ventilation, bypassed by switching to a parallel line, or if it cannot be repaired or contained, maintenance will be summoned (must be priority task).

If CO concentrations are high enough to create an acute exposure hazard, the warning lights should flash. This indicates that a respirator is insufficient for adequate protection, and a supplied air respirator is required. However, this condition should be very rare. As discussed previously, for open process areas, a permanent monitoring system is not practical. The monitoring must be done manually, with a portable gas analyzer. For the purpose of profiling process areas where CO or H_2S is to be used as an indicator gas, respirators must be specifically assigned to an employee or employees on each shift. Essentially, this constitutes a manual leak test program. The instrument sensor should be maneuvered around all potential sources of leaks (flanges, valves, sample pots, etc.). Leaks will be indicated by any instrument reading above the normal background CO or H_2S level, and they can be located and corrected before they become larger and pose a significant employee exposure. As explained before, wearing of respirators may be required until the leak can be repaired, contained, or bypassed.

What if leaks occur while the leak-testing employee is not in the area? First of all, the leaks detected by this method will generally be small and develop gradually. Larger leaks will be apparent, either visually or by a drop in operating pressure, or by the fires they cause. This method is certainly not perfect, but it is acceptable because the frequency of the search cycle in each area will be high and leaks will thus be identified soon after they occur.

This approach to monitoring is used extensively and successfully in the polyvinyl chloride industry. It has considerable merit because it not only provides an indication of employee exposure, but also assists in the control program and determines periods when respirators are required. In some ways this approach is superior to standard personal monitoring. For instance, personal sampling yields no information on what the sources of exposure are and when the exposures occur.

Of primary concern is the potential for airborne exposure to carcinogenic compounds. The indicator gas monitoring system provides some indication of exposure but, because of the importance of this exposure, personal monitoring for benzene soluble fraction of total particulate matter (BSFTPM) is necessary. Workers in each job classification should be periodically monitored. In the initial stages of the program, the frequency of personal sampling should be relatively high. At least for the first several months, an employee in each classification should be sampled once a week. Based on the results of these tests the frequency may be increased or reduced. Because of the large number of maintenance workers, the relatively high potential of exposure, and the variability in their work routines, this job classification should initially be monitored on a daily basis.

When the sample is collected, the worker should be questioned concerning his location during the shift, what tasks he was involved with, and any unusual conditions during the sample period. This information must be recorded to allow an analysis of the sample result. It should be noted that employees working in the coal handling or preparation areas should be exempt from this type of sampling. This is because coal dust contains benzene solubles and thus the result would not necessarily be indicative of actual exposure to carcinogenic compounds. Personal sampling in these areas should follow NIOSH recommendations for evaluating exposure to airborne coal dust.

Periodic personal sampling should be undertaken to determine the efficacy of the indicator gas strategy. Personal samples for toxicants such as benzene or toluene are recommended for each job classification (in areas where these vapors may be present) initially once a month. If, after several months, it is apparent that exposures are low (e.g., consistently lower than one-half the respective standards), the sampling frequency may be reduced to a quarterly cycle.

Some toxicants may be unique because of their probable location and/or toxicological properties and need to be investigated separately. A good example of this is the potential for nickel carbonyl exposure in the methanation area or trace metals in areas where reactor char and ash may become airborne.

MISCELLANEOUS

Physical Stresses

Relative to the health hazards posed by toxic chemical agents, employee exposure to physical stresses such as heat, noise, and vibration is not so severe. However, the potential for problems cannot be neglected.

Sound level readings (dBA) should be taken and recorded for all plant areas, with a properly calibrated sound level meter. All areas having steady-state noise levels over 90 dBA should be posted with signs indicating that ear plugs or muffs are required. This should be required even if employees are only in the area of exposure for short periods of time. Even though time-weighted average exposures may be well below the limit, it is prudent to provide protection even for short exposures. The area of most concern is the coal preparation building, because of noisy mills and vibrating screens. When possible, these sources should be controlled by isolation, with acoustical enclosures. However, this may be difficult to implement because of problems with the need for frequent maintenance and dust buildup and a resulting potential for explosions. Since workers spend much of their time in control rooms, these should be acoustically treated to provide relief from high noise levels.

Impact noise and vibration are not anticipated to be significant sources of exposure. Heat stress problems should not be especially significant either, with one exception — those encountered by workers entering vessels or confined spaces. These operations should be surveyed with wet bulb, dry bulb, and globe thermometers and the WBGT index should be calculated. The NIOSH Criteria for a Recommended Standard — Occupational Exposure to Hot Environments (National Institute for Occupational Safety and Health 1972c) should be used to evaluate the exposure. If it is excessive, management should implement the control recommendations outlined in this document (that is, reducing exposure time, providing air movement and specific clothing, and reducing temperature and humidity).

Welding

Because there is a substantial amount of inherent maintenance and equipment modification in pilot plant operations, welding operations can involve many workers and, therefore, present potential hazards from metal fumes, toxic gases, electrical shock and the potential for explosion. Much of the steel used in pilot plant equipment is alloyed with toxic metals such as chromium and nickel. Further, torch temperatures have to be very high, and welding and brazing materials may contain an unusual combination of toxic metals. All of this may contribute to a very severe health hazard if proper work practices, eye protection, and local ventilation are not used. Because of the nature of the welding operations, it is essential that only highly trained, certified welders be used. The American National Standards Institute publication, "Safety in Welding and Cutting" (1973), may be used as a guide for proper engineering controls.

PRIORITIES

Not enough is known about the nature and sources of air and surface contamination to attempt even a general analysis of potential engineering and work practice controls on a unit process basis. The potential hazards associated with each unit process have been thoroughly discussed in the "Coal Gasification: Process Discussion" chapter of this document and need not be reiterated. However, it is desirable to determine which areas present high health hazards, particularly which ones contain carcinogenic tars and oils. Clearly, intermittent exposure to coal dust does not have the priority of leaking tars and oils from the pretreater.

There are several provisional high-priority areas:

- Pretreater
- Gasifier
- Venturi scrubbers
- Scrubber surge tanks
- Decanter
- Equipment for ash removal and disposal

There is one item that deserves special attention, although it is not directly related to employee exposure or protection. Coal dust may become airborne continuously from open coal piles and intermittently from various operations including unloading, front-end loader of conveyor transporting, and cleanup. From an employee exposure point of view, this is a low-priority hazard relative to others encountered in the plant. However, if this coal dust is blown or drifts into other process areas, it will have an extremely adverse effect on air monitoring activities. The success of the air sampling program rests heavily on the ability to accurately measure airborne concentrations of BSFTPM. As coal dust in the areas where the samples are taken may render the results meaningless, it is important to institute control measures that will either reduce dust generation at the source or prevent it from entering other process areas.

Possible controls include the following:

- Enclosing coal storage piles

- Keeping open coal storage piles tight and compact

- Shielding or partially enclosing coal transport conveyors

- Enclosing all conveyor transfer points (e.g., bin to conveyor, conveyor to bin)

- Scheduling and requiring periodic cleanup operations to minimize coal accumulations throughout the area

- Wetting and/or removing undesired coal accumulations

MONITORING THE WORK ENVIRONMENT

INTRODUCTION

The normal purpose of monitoring is to learn whether exposure to chemical and physical hazards is within prescribed limits and to trigger corrective action if it is not. There are two types of monitoring:

- Area monitoring: Data is collected on workers' locations during a shift and exposure is calculated from that.
- Personal monitoring: The sampling device is worn by the worker. This procedure provides time-weighted exposure data.

Effective monitoring requires practical methods of sampling that are readily adaptable to industrial environments. Sampling must be oriented towards protection of health rather than accumulation of analytical data.

There are few industrial fuel processes that match the chemical and engineering complexities of the coal gasification plant. Solid, liquid, and gaseous intermediates and effluents associated with various operations within all coal gasification pilot plants can come into contact with the skin and respiratory system. As indicated earlier, there are exposure risks from thousands of different chemicals.

If we assume that occupational exposure standards exist for 200 of these chemicals, there are still many remaining substances for which there are no applicable standards or reliable toxicological data. The carcinogens associated particularly with condensable coal-derived hydrocarbons are an extreme case of multifactorial exposure problems. Even the single category of polycyclic aromatic hydrocarbons, considered separately, is very complex. It could not be fully analyzed, compound by compound, on a routine basis, nor could an analysis be translated into a quantitative index of hazard. The evaluation is further complicated by a wide range of potentiators and modifiers:

- High-boiling compounds in the same fractions
- Compounds such as sulfur dioxide and phenol
- Particulates with adsorbed chemicals

Therefore, the recommended approach is to achieve a simplified exposure approximation by measuring only one or two variables. Being an incomplete solution, this calls for other measures to augment worker protection. These measures should be directed towards preventing and controlling emissions, rather than monitoring exposures, and a strong medical surveillance program should be implemented.

An approach is needed that will simplify the problem by a rational method, without sacrificing worker protection. The important concern in developing guidelines is to work within a margin of safety that can reasonably be expected to cover all probable health hazards and to protect personnel from an undesirable level of risk until adequate information leads to the establishment of safe limits.

Sampling and analytical methods are already available for a wide range of chemical and physical agents. In most occupations, a worker in any single job category is exposed to only one or a few toxic hazard(s), and ways to assess the total effect of multiple hazards have been recommended (American Conference of Governmental Industrial Hygienists 1976). Coal gasification plants present unusual problems that demand a special approach to monitoring. The approach recommended here is based on standard instruments, procedures, and exposure limits and it is believed to offer workers the best practical protection, in light of current knowledge. It is also designed to minimize interference with plant operations.

THE PLANT ENVIRONMENT

The open nature of some coal gasification pilot plants creates problems in obtaining representative and realistic samples. There are difficulties in choosing monitoring sites that will provide an accurate reflection of the hazard level in light of changing environmental factors, especially air movements. The problems are less at the enclosed plants (CO_2 Acceptor, Bi-Gas); furthermore, these processes do not produce the polycyclic aromatic hydrocarbons (PAHs) that are of particular concern.

The process areas in a typical coal gasification facility have both unique and common problems that will influence monitoring strategies. Some of the unique aspects of process areas are described:

- Coal stock piles: Spontaneous combustion that may occur, influencing sampling data from other areas
- Coal preparation: Noise associated with milling; airborne coal dust generated by conveying and crushing procedures
- Gasification feed: Toluene slurry in HYGAS process
- Gasification: Possible high concentrations of carcinogenic materials in the gas stream
- Methanation: Potential for formation of nickel carbonyl during start-up and shutdown
- Waste disposal: Thermal oxidation that may emit SO_2

Exposure to Airborne Material

In an enclosed workplace, the concentration field of a contaminant is often fairly constant during normal operation; there may be hot spots and relatively clean areas, but their distribution does not change much. This means that a systematic sampling plan can adequately describe the exposure of a worker assigned to one place or one who averages the concentration by moving about the area. This is the situation existing only in the enclosed space at the gasification plant.

Most of the potential sources of hazard are in open air and many man-hours are spent outside. A point-source emission from a leak, eddying and dispersing through the plant structure and downwind, will set up a very uneven and widely fluctuating concentration field and the general distribution of this "hazard zone" will depend on wind direction and other factors. Furthermore, small differences in working routine may make large differences in worker exposure. It follows that no practical array of sensors can adequately describe the concentration field and even if it could estimates of worker exposure would be very unreliable. However, detection and measurement of point source emissions are valuable in preventing wide area contamination and for initiating repair operations before major effluent emissions occur.

Personal sampling could help to overcome both difficulties but reliable procedures are available only for certain agents and not individually for the carcinogens that are of major concern.

Exposure by Contact

Skin may be contaminated by contact with either surfaces soiled by leakage or the interior of equipment during maintenance. The hazard cannot be quantified because total exposure depends on chance circumstances. A realistic monitoring program should identify the hazard and quantify potential exposure. This is a check on system integrity. It is also a check on cleanliness and good housekeeping.

Physical hazards such as heat and noise can be dealt with as in other occupations, and there are many chemical hazards for which OSHA standards provide a working basis: e.g., for carbon monoxide and hydrogen sulfide. There is a possible complication here in multifactorial exposures, where a simple additive approach may not be justified; however, in the present state of knowledge, no alternative is available.

THE INDICATOR SUBSTANCE CONCEPT

A complete monitoring program must serve two purposes:

- To provide the information required to keep employee exposure at safe levels, using techniques suitable for pilot plant conditions and personnel
- To accumulate data to support the design of engineering controls to be incorporated into demonstration and commercial gasification plants

The approach proposed here recognizes the need for a simple index to serve the first purpose and it will provide useful data for the second. In this approach, a single substance acts as indicator for all the components of a given process stream. The assumption is made that any leak of the indicator substance will be accompanied by a leak of each toxic constituent in the same ratio as in the process stream, so that a measurement of the indicator substance can do duty for individual measurements of each toxic emission. It is recognized that this assumption may not always be valid and that it cannot always be checked by experiment.

Indicators should have the following characteristics:

- Easily monitored in real time by commercially available personal or remote samplers
- Suitable for analysis where resources and technical skills are limited
- Not present in ambient air at high or widely fluctuating concentrations
- Free from interfering substances in the process stream or ambient air
- A regulated agent, so that the measurements serve two purposes

Leading candidates for the indicator substance are carbon monoxide and hydrogen sulfide, as one or the other is always a major constituent in gaseous streams and both meet the criteria.

The rationale for adopting carbon monoxide (CO) as an indicator gas for monitoring in confined areas and as the basis for alarm mechanisms in selected areas is illustrated in Table 28. It can be summarized as follows:

- The concentration of CO is higher than that of other vapors and gases of interest — NH_3, H_2S, and coal tar volatiles (BSFTPM).
- Available alarm and monitoring instrumentation can detect CO concentrations of approximately 0.2 mg/m^3.
- Assuming that emissions from the gas stream will contain the relative concentrations of CO to the other gases and vapors, the approximate level of these can be calculated.
- When calculated, these levels can be compared to existing exposure standards.

Table 28 illustrates that CO serves as an adequate indicator of potential hazard from process stream leakage in all areas except the pretreater, where the benzene soluble fraction is indicated to be above exposure limits.

Although benzene soluble material is the major concern, it is not feasible to choose it or a component of it as an indicator. Quick-response monitors at the necessary sensitivities are not available for these compounds.

Carbon monoxide in particular should be an excellent indicator of system and unit operation gas leaks throughout most gasification and downstream processes. The level of CO at points of fugitive emissions (flanges, pumps, seals, etc.) is high enough that it can serve as an effective indicator for the presence of other toxic gas stream agents.

Table 28. Ratio of CO to some gas stream components.

Stream Component	Pretreater	Gasifier Outlet	Venturi Outlet	Raw Gas Scrubber Outlet	Shift Converter Outlet	Acid Gas Absorber Outlet	Stream to Carbon Reactor
CO_2/CO^a	13.4	3.62	3.63	3.60	6.61	0.10	0.10
Minimum detectable level CO_2, mg/m^{3b}	2.6	0.72	0.72	0.72	1.32	ND[c]	ND
Concentration CO_2 as % OSHA exposure limit	0.03	0.01	0.01	0.01	0.02	ND	ND
NH_3/CO^a	ND	0.05	0.06	0.02	ND	ND	ND
Minimum detectable level NH_3, mg/m^{3b}	ND	0.01	0.01	ND	ND	ND	ND
Concentration NH_3 as % OSHA exposure limit	ND	0.02	0.02	ND	ND	ND	ND
H_2S/CO^a	ND	0.06	0.06	0.06	0.09	ND	ND
Minimum detectable level H_2S, mg/m^{3b}	ND	0.01	0.01	0.01	0.02	ND	ND
Concentration H_2S as % OSHA exposure limit	ND	0.08	0.08	0.08	0.12	ND	ND
Light oil fraction/CO^a	0.32	0.01	0.01	0.01	0.01	0.01	ND
Medium oil fraction/CO^a	1.75	0.04	0.04	0.05	ND	ND	ND
Heavy oil fraction/CO^a	1.28	0.04	0.01	ND	ND	ND	ND
Residual oil/CO (only 50% benzene soluble)	ND	0.05	ND	ND	ND	ND	ND
Minimum detectable level as total benzene solubles, mg/m^{3b}	0.67	0.03	0.012	0.012	0.002	0.002	ND
Concentration benzene solubles as % OSHA exposure limit	335	15	6	6	1	1	ND

[a] Calculations are based on Synthane material balance sheet (Appendix C).
[b] Minimum detectable levels are calculated using 0.2 mg/m^3 as lowest concentration of CO detectable by available instrumentation.
[c] No data.

This method serves several purposes:

- It allows real-time detection of leaks.
- It serves as an indicator for substances that cannot be analyzed in real time.
- It serves as an indicator for substances that are difficult or impossible to analyze at prevailing concentrations.

A comparison of constituents of the overhead gas streams from different gasification unit processes indicates that CO is usually present in high concentration relative to other agents of interest. However, between the pretreater outlet and the gasifier in the example shown, the concentration of condensable hydrocarbons in the gas stream is substantially greater than at any other point in the process. For this reason, CO concentration in any emission from this part of the gas stream will not indicate the presence of benzene soluble material with enough sensitivity. (Fortunately, this is a small, simple vessel and the line is short: extra precautions might be taken.)

Once the gas stream has been quenched in the venturi scrubber, the concentration of CO relative to condensable hydrocarbons will rise significantly as water vapor and condensable hydrocarbons are condensed and removed. Although its concentration fluctuates, CO remains a major constituent of the primary gas stream until the final methanation step, which upgrades the gas to pipeline quality.

An area where a different indicator species must be employed downstream from the acid gas separator, is the sulfur recovery unit. The gas stream in this operation contains a high concentration of H_2S and little, if any, CO. Thus, the most suitable indicator will be H_2S.

A significant consideration is that as the quality of the gas improves from operation to operation, the CO concentration decreases. This decrease is accompanied by an even greater reduction in the other toxic components. The CO monitoring system is therefore most sensitive to a given leak rate where the impact of a leak is most serious, and the probability of false alarms from leakage of "clean" gas is diminished.

SAMPLING METHODS

Surface Contamination

If the contaminant contains condensed polycyclic hydrocarbons, search of surfaces with a handheld UV lamp will make it visible by fluorescence. This may be most conveniently done at night, with any nearby lamps temporarily turned off or shaded. Alternatively, a portable, battery-operated ultraviolet lamp (longwave and shortwave) could be used in a fabric-skirted box to permit surface viewing in a brightly lighted environment. Problems stemming from individual variation in dark adaptation and color sensitivity could be avoided by using a photovoltaic detector and meter readout of fluorescence emission intensity per ft^2 of surface.

Hazards inside equipment may be anticipated from knowledge of the process stream's constituents. Finally, a UV scan of workers' clothing will indicate whether the risk of contact contamination is real. This very nonspecific test does not indicate either whether the compounds causing the fluorescence are carcinogenic or whether a carcinogen might be present that does not fluoresce. The general rationale, however, is that since the class of PAH compounds as a whole exhibits fluorescence and members of the class are known to be carcinogens, this test gives an indication of the presence of suspect agents.

Personal Monitoring

It is recommended that the special problem of high-boiling carcinogens be dealt with in the same way as coke oven emissions are dealt with in Title 29 CFR 1910.1029 (Federal Register 1976a); that is, they should be measured in aggregate, together with other benzene soluble compounds, as the benzene soluble fraction of total particulate matter (BSFTPM) (see Appendix D).

The referenced standard presents the argument for preferring this measure to alternatives such as using respirable particles as a basis or analyzing for benzo[*a*]pyrene as proxy for the whole spectrum of carcinogens (Federal Register 1976a). The standard is supported by epidemiologic evidence, which is not available for gasification plants. In the absence of a better basis for prescribing an exposure limit, it is proposed to assume that benzene soluble matter found in gasification plants is sufficiently similar for the coke oven standard to apply.

No exposure limits can be recommended for substances that may enhance carcinogenicity. The effect may be significant but the required evidence is lacking. However, it is recommended that efforts be made to minimize exposure to known categories of enhancing agents wherever exposure to carcinogens is likely. These categories include skin irritants, lung irritants, mineral particles, and chemical potentiators such as phenol and dodecane.

ANALYTICAL METHODS

It is recommended that standard analytical methods, already approved or recommended for other applications, be used whenever practical, e.g., for CO and H_2S; and that advances in technique be incorporated as appropriate, e.g., in analysis of the benzene solubles.

Analytical methods and instrumentation for CO and H_2S monitoring are well developed. These systems can provide the necessary sensitivity and reliability for implementing the indicator substance concept.

Real-time remote sensing apparatus and portable handheld monitors operating in a variety of modes are available from several sources. These are presented in Appendix C.

Schulte et al. (1974) have considered a number of published analytical methods for applicability to analysis of benzene solubles, PAHs, and B*a*P as obtained from coke oven emissions. Benzene soluble extract was determined based on a weight difference of a filter before and after Soxhlet extraction with hot benzene. Comparison was also made with PAH content (14 compounds) as determined by gas chromatography and with BαP separated using thin layer chromatography and measured fluorometrically. They found a high degree of correlation between BαP concentration and benzene soluble concentration when samples were collected by a high volume (HIVOL) sampler and the horizontal elutriator.

The gas chromatographic (GC) determination of PAH compounds did not correlate well with benzene solubles. It is possible that analytical methods based on gas chromatography introduce opportunities for material losses or gains and chemical reactions ultimately affecting the "signal" ascribed to BαP. Oxidation of PAHs becomes much more significant with increasing duration of exposure to light, air, and heat (Lannoye and Greinke 1974).

Particularly significant to this document is the finding that BαP by thin layer chromatography (TLC) is highly correlated with the benzene soluble content of particulate matter collected on either a high-volume sampler or a horizontal elutriator (Schulte et al. 1974). Extremely poor correlation was observed between all methods for BαP and benzene solubles from samples collected with cyclones or membrane filter field cassettes.

Although the authors of the NIOSH study chose not to speculate on the manner in which methodology affects sample composition, it is possible that some selection process operates where either air washing of volatiles or filter fouling occurs. High surface area collectors, e.g., glass fiber filters, permit greater air washing of the trapped particulate matter during collection, and it is not surprising to lose more volatile "benzene solubles" relative to less effectively air-washed systems or fouled filter systems.

Results have been published of studies on the problems associated with Soxhlet extraction for determining coal tar pitch volatiles (CTPVs) (Seim et al. 1974). They showed that weight loss errors can be appreciable when ultrafines are present (as in aluminum smelter operations). Adipates or other plasticizers in membrane filter cassette housings add to the weight loss noted after Soxhlet extraction. Units with polystyrene housings are preferred over those with cellulose acetate or polypropylene housings.

It is not proposed at present that BαP be monitored as part of the worker protection program. If it is required as part of a research project or in a future modification of the program, recent advances in technique may be applied. Although BαP exhibits violet fluorescence, the protonated species exhibits a bright green fluorescence, which is used in the APHA tentative method for BαP. The protonated species is formed in concentrated sulfuric acid. Lannoye and Greinke (1974) have suggested many improvements in the APHA tentative method for BαP. By implementing these suggestions into the procedure, it is possible to obtain a relative standard deviation of 3.5% to 6.2% over the range from 14 to 400 μg BαP. However, their implementation requires both exceptional analytical capability and an exceptional laboratory facility, not normally available at a coal gasification plant. It may also be noted that PAHs in coal dust could interfere.

MEDICAL MONITORING

SCOPE

This chapter discusses and recommends medical monitoring procedures for workers at coal gasification pilot plants. It is directed to the physicians responsible for monitoring and also to others, such as plant management and policy makers, who wish to understand the general purpose and nature of the recommended medical procedures. Consequently it is written for a dual audience. For example, respiratory function tests are recommended, specifically FVC and FEV_1. "Respiratory function" explains it sufficiently for the layman and there is no need to expand on FVC and FEV_1 for the physician.

The chapter on health effects has identified known and suspected toxic agents and their health effects. Heat and noise stresses have also been discussed. The more conspicuous toxic hazards include polynuclear aromatic hydrocarbons and other carcinogens such as β-naphthylamine and benzidine, nitrosamines, and possibly nickel carbonyl. Compounds capable of potentiating carcinogenesis include acridines, dodecane, sulfur oxides, and other irritants such as phenols. Organs conspicuously at risk are the skin, the lung, and other parts of the respiratory tract and the genitourinary system, especially the bladder.

Effects other than cancer are significant. The skin may develop dermatitis or photosensitization. Nonmalignant respiratory effects include chronic bronchitis, emphysema, and possibly pneumoconiosis. The liver and central nervous system (CNS) may be at risk from aromatic amines such as aniline. CNS effects are induced by phenols, carbon disulfide, and carbonyls. A highly specific hazard is benzene, which is myelotoxic and leukemogenic.

Mutagenic and teratogenic effects are a possibility which must be borne in mind because of the serious consequences. Exposure to some suspect classes of compounds is possible.

The purpose of the foregoing very brief review is to help focus on the major targets for medical monitoring and to identify the organs at risk. This supports an orderly and convenient approach to medical monitoring on an organ-by-organ basis.

It should be borne in mind that the discussion and recommendations are generalized for all coal gasification plants. The physician at any particular plant must consider what specific exposures might be expected. These can be identified from chemical engineering data and perhaps workplace monitoring. He should also consider individual risk of exposure based on job description. This kind of information will permit tailoring of medical tests: for example, possible exposure to aromatic amines should suggest addition of a liver function test to the recommended basic examination.

OBJECTIVES

A preemployment physical, routine checkups, and a physical on termination are common practice in industry. Medical monitoring has considerable added importance at coal gasification plants because it is not possible (and may never be possible) to assure "safe" exposure by application of controls or environmental monitoring. Another reason is that health effects may show up after a long latent period, perhaps long after exposure has ended. A third reason is that some of the possible ill effects would develop inconspicuously at first; that is, they would not clamor for immediate attention. Consequently, regular and continued medical monitoring is needed as a warning system, so that emerging problems will be dealt with at the earliest possible time.

The primary purpose of medical examination is to protect the examined worker's health, during a period of occupational exposure and thereafter. There is also a valuable by-product in that medical records will help to protect the health of other workers, at different plants and in the future. Accumulated knowledge of occupational health is the best input to development of recommended procedures for protection of workers' health. Medical records and associated histories of working exposure should therefore be prepared and held with this in mind. Development of the present document would have been considerably helped if past records and follow-ups had not been scanty or nonexistent; although the recommendations might not have been different, they would certainly have rested on more solid evidence.

In summary, the recommended scope of medical monitoring includes:

- full preemployment physical, including history and laboratory tests, which serves three purposes — a general check on fitness, identification of high-risk individuals so that they may be advised, and a baseline for further routine examinations;
- regular checkups, more frequently and in more detail for high-risk individuals (those with 5 years of exposure or over 45 years of age);
- long-term follow-up of high-risk individuals after transfer to other job categories for termination; and
- full record keeping, including work history and exposure data.

It should be remembered that full medical surveillance requires good liaison between the occupational physician and the individual's private practitioner, so that untoward signs may not be neglected.

MONITORING NEEDS

As Dixon (1973) has emphasized, "Humans want to be medically tested rather than biologically monitored" and measuring only the "health of the air" is unsatisfactory. Bioassay and area monitoring alone are clearly not sufficient. When one reviews the natural history of the development of cancer (Kotin 1976), the need for medical surveillance is obvious. The time, place, or amount of exposure which causes the initial interaction between the carcinogenic agent and the host cannot be precisely determined. No specific biomedical markers can be identified in tissues indicating that initiation has occurred. When tissue responses become detectable, they are usually nonspecific and often not pathognomonic. Once initiation and even transformation have occurred, a long latent period, sometimes lasting 20 to 30 years, occurs. During this time other factors, such as age, sex, genetic abnormalities, exposure to promoters or to hormonal agents, and injuries which cause tissue proliferation may determine if cancer will ever appear. Under such circumstances, only periodic clinical evaluation will determine if exposures are causing an increased incidence of tumors.

Medical monitoring is also an essential part of worker protection against the consequences of chronic exposure to noncarcinogens.

A relatively small number of workers (probably less than 5,000) have been employed at coal conversion pilot plants in the United States during the past 20 to 25 years. They have not been carefully monitored and their exposures may have been fairly high. Even though their future exposures may be at "safe" levels, the effects of past exposures must be followed. Since what is "safe" is not known, it would also seem prudent to monitor new employees under new working conditions very thoroughly until enough experience has been obtained for management to be comfortable in reducing medical surveillance procedures.

A part of worker protection must come from adequate follow-up after exposure in hazardous areas. The information gained in this as well as routine occupational examination should be used not only for the workers' immediate protection but also to enhance knowledge generally for the protection of others.

The value of all medical monitoring in its broader application will be enhanced by having suitable control populations, followed in a closely similar manner. Offering the same surveillance program to all employees at a plant has obvious advantages for employee relations and may incidentally furnish an adequate control population even if the numbers are relatively small and their characteristics do not match closely.

Evaluation of medical records may on occasion be facilitated by comparison with those from other similar locations and this will be more effective if the data have been collected and recorded in the same way. Uniformity would also permit aggregation to form a larger and more useful historical data base. In this connection, and also for individual protection in long-term follow-up, it is recommended that a national system be set up to preclude loss or inaccessibility of records if, for example, a plant closes.

EFFECTS ON ORGAN SYSTEMS

Possible health effects are reviewed here with reference to the affected organ system. This is for convenience in developing medical monitoring procedures for specific circumstances, in conjunction with reference to the presentation of health effects by specific compounds in an earlier chapter.

Skin Effects

Nonallergic dermatitis, cell-mediated hypersensitivity, cutaneous photosensitization, acne, premalignant lesions, and malignant lesions have been associated with PAH exposures (National Academy of Sciences 1972). At the Union Carbide plant in Institute, West Virginia, skin cancers and premalignant changes were seen sometimes after a remarkably short latent period of less than 5 years (Sexton 1960b). Since these changes are not specific and a possible association with occupational exposures could easily be missed in random observations by scattered individual private practitioners, close medical surveillance by one or very few trained and interested observers is necessary. Longitudinal observation over a period of years enables a skilled physician to become familiar with the texture, appearance, and disease problems of the skin in a small group of workers.

Appearance of skin cancer may be a warning sign for later cancer in the respiratory and upper digestive tracts. Holmes et al. (1970) reported a significant association of these effects in men who had had scrotal cancer. This is an important point in follow-up of cases.

Noncarcinogenic skin effects that may be encountered in exposure to agents other than PAH are irritation and sensitization.

Lung Effects

The National Academy of Sciences (1972) stated that "in no instance has exposure to a specific polycyclic aromatic hydrocarbon been proved to have caused a tumor in man." Although this is strictly true, the evidence of an increased risk of lung cancer in coke oven and roofing workers exposed to PAH is impressive (Menck and Henderson 1973; Lloyd 1971) and medical surveillance is clearly obligatory.

PAH compounds in coal conversion processes may be adsorbed on fine particles, a good portion of which may be 0.5 μm to 2.5 μm in diameter and therefore "respirable." It has been shown that many inhaled compounds can have a ciliostatic effect, which could increase the length of time of exposure in the lower respiratory tract. Even if particles contaminated with tars are cleared fairly rapidly from the respiratory tract, leaching has been shown to occur, which suggests that the PAH material is retained even though the particle may be cleared. The fate of the leached material is still unknown (National Academy of Sciences 1972). In animal experiments, inert particles such as hematite (Saffioti et al. 1968) or carbon (Pylev 1967) have had to be inhaled in order to produce lung cancers.

Among other effects is acute irritation, which may be caused by a wide range of possible emissions (ammonia, hydrogen chloride, sulfur oxides, nitrogen oxides, phenols, etc.) and might be associated with cancer promotion. Acute and chronic respiratory dysfunctions are known effects of some trace elements which are likely to be present, especially vanadium and also beryllium, cadmium, and manganese. Dusts of silica, limestone, and coal can induce pneumoconioses.

Urinogenital Effects

An excess of bladder and kidney cancers has been reported for workers exposed to coal gas, tar, and pitch (Redmond et al. 1972; Doll et al. 1965). These tumors are relatively rare and have a long latent period. Early detection and treatment usually improves the prognosis. A requirement for medical surveillance using urine cytology has appeared in the Coke Oven Emissions Standard (Federal Register 1976b).

A range of aromatic nitrogen compounds has been shown to cause kidney injury. Several of the possible trace elements have been similarly implicated: beryllium, cadmium, lead, mercury, and selenium.

Blood and Blood-forming Tissue Effects

Leukemia and myelotoxicity are associated particularly with exposure to benzene (NIOSH 1976a). Carbon monoxide induces carboxyhemoglobinemia and aniline induces methemoglobinemia. Anemia is a characterisitic sign of lead and selenium poisoning.

Cardiovascular Effects

Chronic exposure to carbon monoxide has been said to cause or aggravate cardiovascular disease. Carbon disulfide has similarly been implicated in cardiac disease and hypertension. Among the trace elements, chronic mercury poisoning is characterized by cardiovascular disease and other effects.

Liver Effects

Aromatic amino compounds (e.g., aniline) and N-heterocyclic aromatics (e.g., pyridine) are possible sources of hepatotoxicity among coal conversion products if exposure is high enough. Liver function and serum transaminase tests should be considered for inclusion in routine examinations if this is suspected. Among the trace elements, beryllium and selenium affect the liver.

Central Nervous System Effects

Carbon monoxide at a sufficient exposure level may produce characteristic and reversible signs of hypoxia; no persistent effect on the CNS has been proven, short of damage through severe hypoxia. Several other possible contaminants induce acute and probably reversible CNS effects: hydrogen sulfide, carbon disulfide, carbonyl sulfide, phenols, and carbonyls. Prolonged or permanent damage may be associated with chronic exposure to lead, mercury, and selenium.

PREEMPLOYMENT ASPECTS

Acquiring knowledge of the general health status of prospective employees is prudent for several reasons. In addition to the usual criteria of physical fitness, individuals with blonde or red hair and pale complexions will need to be evaluated for high risk of skin cancer. Individuals with existing chronic lung disease or marked atypia in cells exfoliated from their bronchial mucosa may have enhanced susceptibility to lung cancer. Individuals with abnormal urine cytology or a history of a bladder papilloma or tumor will need to be evaluated for risk of carcinoma of the bladder or urinary tract.

A preemployment examination provides an important baseline for future examinations. For this reason, as well as the high-risk indicators just mentioned, it is essential for the examiner to be aware of the special purposes of the examination and the nature of possible health hazards. Since pilot plants usually do not have their own occupational health physicians and are likely to depend on outside general practitioners, transmission of the necessary information should be a stated responsibility of plant management. A point to be emphasized is the desirability of obtaining as full an occupational history as possible, including past exposures to chemical and physical stresses, and also details about smoking and drinking.

The Federal Register (1976a) contained a recommendation for both urine and sputum cytology for coke oven workers. The former is more generally accepted as a routine monitoring tool, but only if the preparation and evaluation are done expertly and by established methods. Sputum cytology is more controversial and more likely to be misleading unless in expert hands. However, both techniques have the obvious advantage of generating a permanent record (microscope slide) that can be reexamined.

Sputum cytology may be performed according to the technique of Saccomanno et al. (1974). The cytologist must be experienced in classifying degrees of atypia. The sputum may be collected spontaneously if the worker can produce a deep-cough, morning specimen. Sputum induction, using inhalation of a fine aerosol of 20% propylene glycol and 15% saline, can provide an excellent specimen. At least two sputum cytology studies should be performed to assure an adequate sampling of cells exfoliating from the bronchial mucosa. Individuals with marked atypia (or, of course, those with carcinoma in situ or invasive carcinoma cells) should be carefully evaluated before being employed. Those with marked atypia who are cigarette smokers are at increased risk of developing a future lung cancer.

OCCUPATIONAL AND POSTOCCUPATIONAL ASPECTS

The physical examination should pay particular attention to the skin. Actinic effects and the presence of benign or premalignant lesions should be carefully noted. Suspected malignant lesions should be removed and their histology documented. A high quality, close-up color photograph (slide) of the skin, especially of the face, neck, and hands, is probably the only adequate way of documenting the appearance of the skin. The lungs should be evaluated for the presence of rales or rhonchi, suggesting a chronic bronchitis. A general examination should be carried out.

Laboratory studies should include posteroanterior (PA) and lateral (14" x 17") chest X-rays, weight, pulmonary function (a minimum of FVC and FEV_1), and a routine urinalysis. An ECG and multiple serum chemistries are desirable, especially if the applicant is over 40.

The frequency and extent of examination should reflect the degree of need, which depends on duration and extent of past exposure, expected future exposure, and personal characteristics such as age and medical history. The skin should be examined at least once a year, preferably during the winter months when effects of current ultraviolet light exposure are less apparent, but complete physicals might be acceptable at less frequent intervals for low-risk individuals. Recommended schedules are given in the next section of this chapter.

A termination physical examination with the same content as the regular complete examination should be performed when a worker leaves if a complete examination has not been performed in the preceding year.

RECOMMENDED PROCEDURES AND SCHEDULES

It is recommended that a preemployment medical examination be required for all before hiring. All workers should be offered regular examination and a signed statement should be obtained from those who refuse it. Individuals judged to be at significantly higher than average risk because of personal factors, work history, or expected future exposure should be advised by a physician before signing the release.

Basic Procedures

The following should be included in the initial examination but not necessarily in all subsequent examinations: skin examination; X-ray, 14" x 17" PA and lateral; FVC and FEV_1; weight; blood chemistry; urinalysis including test for hematuria.

Additional Procedures

It is recommended that consideration be given to additional procedures such as an ECG, especially for high-risk individuals. Exposure to certain toxicants calls for special procedures: e.g., liver function test for workers exposed to aromatic amines.

The recommended basic and additional procedures are not intended to exclude further tests. The physician will of course consider other aspects such as physical fitness for heavy manual work.

Schedule for Normal-risk Individuals

This applies to all exposed workers except the high-risk category defined below. Annual examination is recommended, to include: skin; X-ray; FEV and FVC_1; weight; urinalysis; cytology.

Schedule for High-risk Individuals

Workers who have accumulated 5 years of exposure or are over 45 years old should be considered as a high-risk group. The job categories which constitute "exposure" must be determined in the light of environmental monitoring records, work practices, prevalence of leaks, etc. Six-monthly examination should include: skin; FEV and FVC_1; weight; serum analysis; urinalysis; urine cytology; sputum cytology. X-ray examination should continue to be annual.

RECORD KEEPING

Medical Records

Following are the minimum recommended scope and duration for keeping medical records on file:

- Medical history on employment: 40 years
- Initial X-ray and cytology slides: 40 years
- Abnormal X-ray (if any) and all subsequent X-rays: 40 years
- Cytology slide showing atypia (if any) and all subsequent slides: 40 years.
- All X-rays for the last 5 years and cytology slides for the last 10 years

Exposure Records

The physician responsible for filing medical records should obtain from the plant management, and file with the relevant medical records, a record of each worker's job history. This work record should be adequate to support an estimate of level of exposure and nature of toxic or physical agents involved. Adequacy will depend on circumstances; suggested criteria include the following:

- Full history of workstation assignments exceeding 1 month, for single-station workers
- Principal areas of work, for mobile workers
- Work history obtained at preemployment or other examination or interview

Summary Reports on Environmental Monitoring at Relevant Workstations

The full monitoring data should be kept on file but preferably not with the medical records; the summary reports are necessary to determine whether the environmental data files should be searched in event of a retrospective investigation.

Special records of heavy exposure to substances retained inside equipment may be desirable when maintenance operations are carried out or when modifications are implemented. The decision to include these would depend on identification or strong suspicion of the presence of toxic hazards, as determined by chemical analysis or biological test.

Exposure records should be kept as long as medical records; i.e., 40 years.

SAFETY

INTRODUCTION

The development of recommended safety guidelines for coal gasification pilot plants is complicated by the great variety of processes and facilities planned and now in use as well as by the dearth of information available on existing safety procedures. This situation makes necessary a process-by-process overview of hazards followed by comprehensive safety program recommendations that take into account applicable existing regulations.

In general, process development or pilot plant installations present more unpredictable hazards than fully tested production-scale facilities, simply because they are essentially large laboratories where equipment and process conditions are examined on an experimental basis. As a consequence, operations are cycled up and down frequently and the plant as a whole is shut down for maintenance much of the time while equipment is inspected, repaired, modified, or replaced. Hazards encountered during maintenance are always a major concern in large chemical plants. This problem is accentuated in pilot facilities. Further, the many process variables encountered in pilot plant production runs may contribute to unusually high vessel and piping erosion rates as well as unexpected overpressures and overheating.

This chapter will attempt to identify the hazardous conditions that may be present in a typical coal gasification pilot plant and will present recommendations for control of these hazards. Alternative safety implementation programs and their relative merits will also be discussed.

OVERVIEW OF HAZARDS

The first unit operation encountered in the coal gasification plant is coal crushing and grinding. This is usually accomplished in a dry mill at feed rates of up to 5 tons per hour. In operations that do not dampen the coal in the crusher to minimize dust, the grinding areas may show substantial concentrations of coal dust in the air, and surfaces in the vicinity will be subject to dust buildup.

Such conditions can result in the possibility of a deflagration of suspended dust and of subsequent deflagrations of dust dislodged from rafters and other surfaces. The likelihood of coal dust explosions is dependent on several factors, among them the presence of a suitable ignition source, the type of coal used, the coal's moisture content, the particle size and shape, uniformity of dust particle suspension, and ratio of dust concentration to oxygen content of the gas. The most hazardous form of coal dust found in these operations is fines from heat-dried lignite, which is highly pyrophoric in air; however, there is a hazard in the use of other coals such as bituminous, sub-bituminous, and anthracite.

The next process downstream in certain operations is pretreatment of the crushed coal prior to its introduction into the gasifier. Here the coal is heated to around 800°F (545°C) while blanketed with recycled gas and/or steam. Sufficient air is metered in to maintain temperature. The major hazardous condition at the pretreater occurs when samples of coal from the pretreater are collected. This is done by opening a valve in the bottom of the pretreater vessel and handling the hot coal in a sample can. There is, therefore, the hazard of burns either from direct contact with the hot coal and sample can or from the fire that may result if hot pyrophoric coal is spilled because of sample valve failure. Coal samples from the pretreater are collected from once a day to as frequently as several times per shift to determine the moisture content and overall quality of coal going into the gasifier.

Some gasification processes require that oxygen be metered into the gasifier to maintain process temperatures. Liquid oxygen is trucked to the site and stored in tanks adjacent to the process area, prior to being vaporized and introduced under pressure into the gasifier. The hazards associated with handling liquefied oxygen are well known and safe work practices have been developed (The Applied Physics Lab 1963). The major on-site hazards are accidental overheating and rupture of the oxygen tank, and failure of automatic controls, due to the excess oxygen metered into the gasifier.

The primary fire hazard in the gasification process is the gasifier unit, because of the high pressures and temperatures at which it operates combined with the combustible and abrasive nature of the gasifier effluents. Pipes carrying crushed coal or char into or out of the main gasifier vessel are particularly susceptible to erosion, overheating, and rupture. Such ruptures force hot process gases into the atmosphere at high pressure. These can ignite immediately, resulting in dangerous but largely self-contained gas fires. Additionally, the escaping gases can drift several hundred feet before ignition, creating a serious explosion potential. The routine procedure of manually sampling gasifier bed solids is particularly vulnerable to starting leaks. This sampling procedure may be accomplished by screwing a steel cylinder "shot pot" onto a sample tee, opening a valve, and allowing the cylinder to fill with solids. The valve is then closed and a cooling down period of 40 to 60 minutes is allowed, after which a valve in the bottom of the cylinder is opened and the solids are collected in a sample can. If the valve at the sample tee has failed to reseat properly because of the intense heat, process gases may then escape into the air and ignite, presenting a hazard to workers in the area. Use of a double valve sample train eliminates many of the leak hazards.

Failure of automatic process control systems may also result in hazardous conditions, especially if failure results in overheating of vessels and piping due to insufficient water jacket cooling or introduction of excess oxygen into the gasifier. However, redundant instrumentation and "fail-safe" design can reduce these hazards to a negligible level by providing for emergency shutdown when process parameters exceed preset limits.

Downstream of the gasifier is product gas quenching and scrubbing, described in detail in the chapter on processes. During normal operations samples of quench water are taken manually about once every shift. This can be a hazardous procedure, as hot quench water spilling on exposed skin can cause burns.

In the remaining downstream processes of shift conversion, acid gas scrubbing, sulfur removal, and methanation, highly combustible gases are being processed. The possibility of these gases' escaping into work areas creates potential for fire, explosion, and acute toxicity (e.g., CO and H_2S).

Many potentially hazardous conditions exist in pilot plants because of the frequent maintenance and process equipment modification work required as a process is developed. In the following analyses, frequently encountered situations are discussed and general guidelines for safety in maintenance and modification work are presented.

In any maintenance procedure that requires a vessel, duct, flange, valve, pump, or compressor to be opened the potential hazard is present for the release of toxic and/or combustible gases or solids into the work area. Many factors contribute to the possibility of such a release, especially the incomplete isolation and purging of the involved system prior to its opening. Even when a thorough purging of gases is carried out, workers entering the vessel or piping may be exposed to toxic and/or combustible mixtures because of adsorbed gases from solid particles remaining in the purged space. Pulverized coal or char is a particularly good adsorbent of many gases and its presence in the gasifier vessel contributes to this problem. Tight bends and blind sections of piping can also harbor high concentrations of acutely toxic and flammable gases. Additionally, the possibility of an accidental release of gases from another part of the system into the part undergoing maintenance creates a hazard.

Whenever vessel entry by maintenance personnel is required, there is a potential for simple asphyxiation because of the lowered O_2 concentrations. Heat stress may also occur if the vessel has not cooled completely to ambient temperature. (A gasifier that normally operates at 3000°F will require at least 3 days to cool down to ambient temperature.)

Welding and cutting operations can be particularly hazardous in coal gasification plants because of the variety of combustible materials in the plant area. Coal dust, process gases, methane, concentrated oxygen, and certain coolants (e.g., diphenyloxide) used in heat-exchange systems all present combustion or explosion hazards, particularly when the ignition source is a 6000°F welding arc or flame.

General safety considerations in maintenance operations include the necessity of properly isolating the work area to prevent entry by unauthorized persons, proper shielding of welding and cutting operations, the provision of easily accessible fire fighting equipment and breathing apparatus, provisions for orderly evacuation in emergencies, and the ready availability of first aid and medical care.

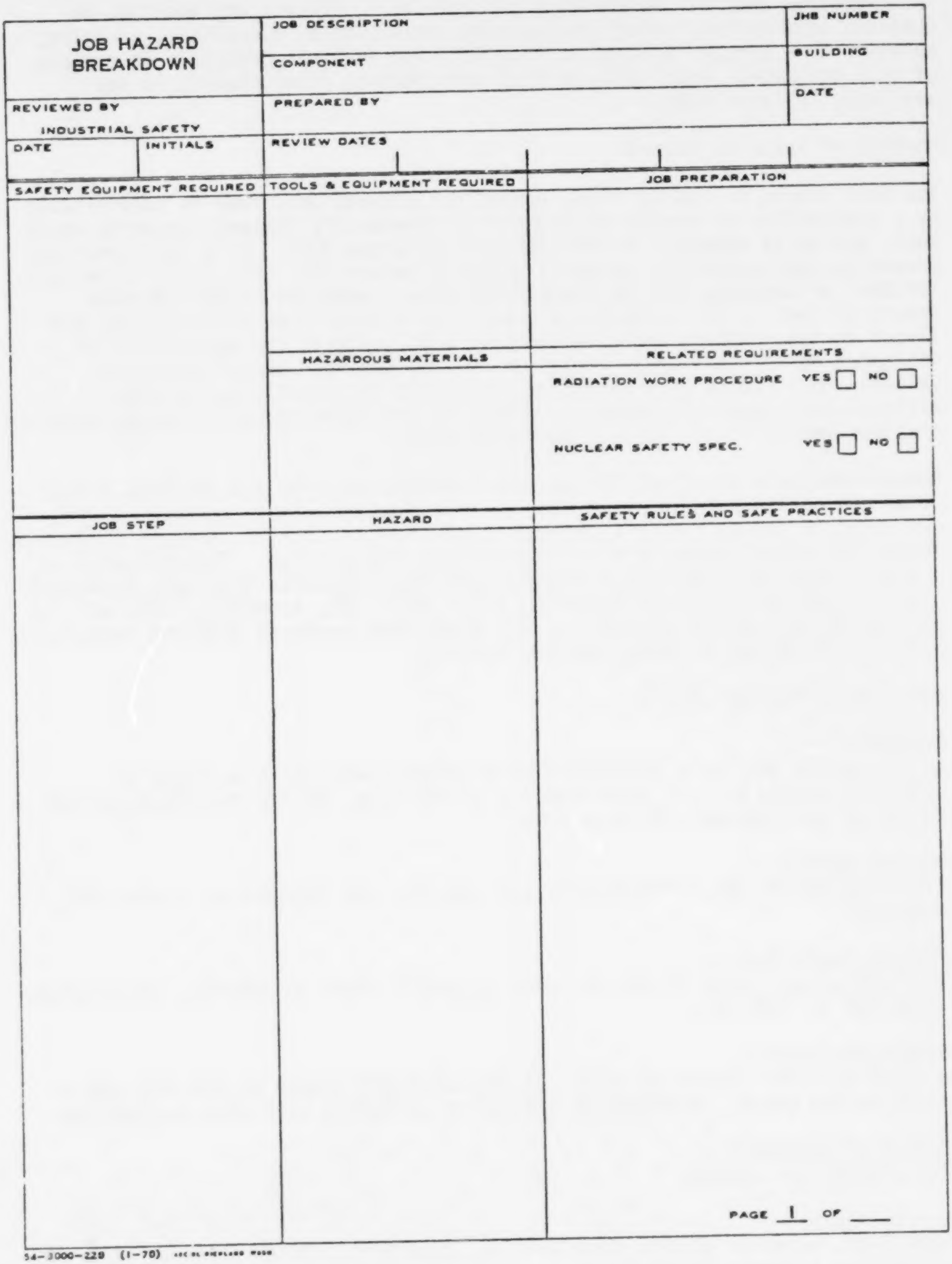
It is absolutely necessary to develop and enforce safe operating practices during start-up and shutdown of the plant. Hazards inherent in start-up include incomplete isolation of the system from its surroundings due to open valves and leaks from flanges, vessel ports, and tie-ins. Such leaks are likely to be found at start-up because maintenance operations are usually performed during shutdown; therefore, the system has been opened; valve position sensors may have been disconnected; and the system may have been incompletely resealed following the work. Hazards arising from shutdown involve the incomplete purging of the system and the possible entrapment of process gases in one part of the system due to faulty valve operation.

RECOMMENDATIONS

General

Recommended safety standards for coal gasification pilot plants will be most effective if a detailed safety clause is included in all labor contracts which specifies the safety regulations and practices that are to be followed and where the responsibility lies for their implementation. This emphasis on safety in contractual agreements should be carried through with the establishment of an independent safety section within the company, with its own budget, and supervised by a competent, full-time professional safety manager who is responsible for the thorough implementation of the safety program. (The part-time employment of safety consultants to fill the post of safety manager or safety engineer is clearly inadequate to deal with the comprehensive safety programs outlined here.) This implementation would include safety analyses at the design stage of the plant, rigorous enforcement of safe work practices during construction, indoctrination of employees via imaginatively designed safety training courses, and use of complete system of accident and "near miss" reporting for internal use. The recording of "near miss" hazardous conditions and minor injury accidents is rarely done in industry but it is essential in pilot plant operations, which have very little previous safety information to work with. Continuing analysis of detailed internal accident reports is particularly important to an effective safety program, as it can allow potential hazards to be identified before a serious accident occurs. Further, a job safety analysis should be conducted by the safety supervisor for each operation in the plant to pinpoint specific hazards unique to each job and to aid in the development of appropriate work practices. Figure 22 is a sample form for such an analysis (Battelle Northwest Laboratory 1976).

Because of the wide variety of processes under development in various pilot plants, it is essential that the managers and operators of each plant have a clear and detailed picture of all potential hazards that exist in each area of the plant. Although many hazards are common to all plants and can be pinpointed and analyzed in a document such as this, only a systematic review of hazards conducted by the operating company, preferably during the design phase of plant development, will give a sufficiently complete overview of problem areas. The analysis should include, but not be limited to, discussion of procedures for operational start-up, normal onstream operation, shutdown, and emergency. The requirement of such a "system safety analysis" will impose a disciplined and inclusive approach to safety considerations. It should assure proper safety engineering in equipment design (MacNab 1975) and eliminate any inconsistencies in the safety equipment or in safety procedures. This type of analysis should be utilized throughout the life of the plant whenever new equipment or procedures are contemplated. (The Fault Tree Analysis for safety and reliability [e.g., the Lapp-Powers Fault Tree Synthesis Algorithm] or its equivalent is recommended as such an approach.)



JOB HAZARD BREAKDOWN

JOB DESCRIPTION

JHB NUMBER

COMPONENT

BUILDING

REVIEWED BY INDUSTRIAL SAFETY

PREPARED BY

DATE

DATE

INITIALS

REVIEW DATES

SAFETY EQUIPMENT REQUIRED

TOOLS & EQUIPMENT REQUIRED

JOB PREPARATION

HAZARDOUS MATERIALS

RELATED REQUIREMENTS

RADIATION WORK PROCEDURE YES ☐ NO ☐

NUCLEAR SAFETY SPEC. YES ☐ NO ☐

JOB STEP	HAZARD	SAFETY RULES AND SAFE PRACTICES

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Figure 22. Job safety analysis sample form.

This requires that all responsible departments — process engineering, mechanical engineering, safety engineering, maintenance, operations, and plant management — become involved in this decision analysis process. An example of this procedure, applicable to coal gasification pilot plants, is now available (Wilson 1976).

Control of Specific Hazards

The dust hazard in coal grinding operations already described is controllable by a combination of careful maintenance of adequately designed crushing equipment, and daily emphasis on wash-down of collected dust. If a coal crushing pneumatic coal conveying system is property maintained, with either a venturi, scrubber or baghouse for the removal of fines, there should be a minimum amount of dust in the surrounding area. Daily spray-down of structures and floors in the crushing and grinding area will minimize the possibility of dislodged dusts creating an explosion or fire hazard. Hinged pressure-release doors should be provided on ducting to the crusher and grinder to minimize the potential danger of rupture in the event excessive oxygen concentrations result in an internal dust explosion.

Recommended safe practices for various sampling start-up and shutdown procedures are outlined in the next part of this chapter. These procedures were described in the course of a personal communication with Mr. Kenneth M. Martin, safety consultant formerly with Stearns-Roger Corporation. The following is a generalization of several different sampling procedures that were developed over a 4-year period at an operating pilot plant (CO_2 Acceptor); they will be implemented at another (Bi-Gas). This experience produced sampling techniques with a high degree of safety and reliability.

Sampling of Reactor Solids

Purpose--
Solid samples are to be obtained from different bed levels in order to determine degree of coal gasification, solids size, solids distribution, and degree of calcination (CO_2 Acceptor).

Process Sample--
Fluid-bed solids are collected through gasifier and regenerator levels (CO_2 Acceptor).

Process Conditions--
The temperature range should be 1500° to 3000°F (814° to 1650°C), the pressure level 150 to 1500 psi.

Sample Container--
A steel cylinder should be used. It has a screwed nipple on one end, and a valve on the other. A prepurged 1/2-gallon container will also be required.

Number of Workers--
Two workers are needed.

Worker Apparel--
Hard hats, asbestos gloves, face shields, coveralls, safety shoes or other protective footwear are worn.

Procedure--
One operator is stationed within 10-15 feet of the sample point near an alarm button. The alarm button activates the emergency shutdown procedure (as described later) in case of mishap. The second operator screws the sampling cylinder onto the sample tee and then opens a manual valve, allowing the cylinder to fill with solids. The manual valve is closed and the operators may leave the area during a cooling down period of 40 to 60 minutes. The operators then return, resume positions, and open the valve at the bottom of the cylinder in order to release the collected solids into the container. The container is then sealed. The cylinder is purged and unscrewed from the sample tee.

Hazards--
Repeated exposure to entrapped gases or vapor may be harmful. Use of an appropriate respirator should be required.

Process gas leaks due to the freezing of valves by intense process heat can be hazardous. Operators should first attempt to close manual backup valves upstream of the sample point. If this is unsuccessful, the hydraulic emergency valve is closed. If this also fails, both operators should leave the area immediately, and activate the alarm to initiate emergency shutdown procedures. Simultaneously, emergency crews are dispatched to the area — dressed in proper clothing — to begin wetting down structures or discharged solids (see later discussion of "Fire").

Hot Coal Sampling

Purpose--
Hot coal analysis.

Process Sample--
Coal is to be collected.

Process Conditions--
Temperature should be set at 500°F (260°C); 10 psi is the proper pressure.

Sample Container--
Prepurged 1/2-gallon can.

Number of Workers--
One worker is required.

Worker Apparel--
Hard hat, face shield, coveralls, asbestos gloves, and safety shoes or other protective footwear should be worn.

Procedure--
The can is placed under the sample tap and opened. Then the process valve is opened for a sufficient time — 15 to 30 seconds — to allow partial filling of the container. The container is immediately sealed and is not reopened until the coal has cooled.

Hazards--
Under these conditions there is a small possibility that the sample will ignite spontaneously. Further, the hot gases at this temperature are predominantly inert, containing little or no toxic material. If the valve should freeze, hot coal will spill onto the floor. This will begin to smolder or ignite after 3 minutes. The sample line should contain a double valve, and a fire extinguisher should be readily available.

Cool or Cold Gas Sampling

Purpose--
To collect product gas analyses.

Process Sample--
Gas streams except methanated gas stream.

Process Condition--
The temperature should be below 400°F, process pressure.

Sample Container--
Evacuated metal sample bottles.

Number of Workers--
One worker is required.

Worker Apparel--
Hard hat, coveralls, gloves, face shield, and safety shoes or other protective footwear should be worn.

Procedure--
Sample container is attached to sample port and container is opened; valve is partially opened to permit container to equilibrate. Close both the sample valve and the sample container.

Hazards--
Inability to close sample valve may result in a container leak, releasing gases to atmosphere and operator breathing zone. The danger of fire is small because of the low volume and low temperature of the gas. If the leak does occur, the operator should put on breathing apparatus (located conveniently to all sample ports) and attempt to plug the leaking fitting. If this fails, emergency shutdown procedures should be initiated.

Quench Water Sampling

Purpose--
To determine process efficiency.

Process Samples--
All water quenching or water scrubbing processes should be sampled.

Process Conditions--
Should be below 110°F (55°C), process pressure.

Sample Container--
A closed can is used.

Number of Workers--
One worker is required.

Worker Apparel--
Hard hat, coveralls, safety shoes or other protective footwear, gloves impervious to aromatic hydrocarbons, and safety goggles should be worn.

Procedure--
Attach sample can to sample port and open can. Open sample valve to partially fill the can. Close valve and cover can.

Hazards--
The primary hazard results from splashing. The quench water will contain contaminants which can cause dermatitis. It may also contain hydrocarbons at low concentrations. In the event of a splash on the operator's skin or clothing, the operator should shower and change clothes.

Slurry Sampling

Purpose--
Stream constituents are to be analyzed.

Process Sample--
Any of the circulating tar streams or gasifier feed streams should be sampled.

Process Conditions--
Temperature should be ambient to 450°F (232°C), and process pressure should be maintained.

Sample Container--
Double-valve metal cylinder is used.

Number of Workers--
One worker is required.

Worker Apparel--
Hard hat, coveralls, impervious gloves, face shield, safety shoes or other protective footwear should be worn.

Procedure--
The metal cylinder is inserted into a line bypass and purged with inert gas. The sampling vessel's valves are opened, while the main line valves are closed. The container is flushed with slurry for 2 minutes, the container valves are then closed and main line valves opened. The bypass is purged to decontaminate the lines, and the container is removed.

Hazards--
If a valve will not close, the sample container is to be left in the system. The primary hazard is from leaking material, which can contaminate both the work space and the worker. In case of severe splashing (union not properly purged, cylinder leaking), the operator should be required to shower and put on clean work clothes.

START-UP AND SHUTDOWN

Safe start-up and shutdown procedures will be discussed together in the following analysis. Pilot plants continually go through cycles of process start-up and shutdown; runs generally last no longer than 2 weeks (7 days at equilibrium conditions), and maintenance and modification are frequent needs. The unusually large number of cycle-up and cycle-down periods, especially when high temperatures and pressures must be reached, creates the need for special safety considerations. Start-up, voluntary shutdown, and emergency shutdown procedures are presented, based upon procedures developed at several coal gasification pilot plants.

Start-up After Extended Shutdown (1 week or more)

System leaks are a major safety consideration in starting up the plant. Therefore, the entire system is gradually repressurized with inert gas (N_2) to about 150 psi (CO_2 Acceptor). At this point, teams of workmen check the entire system for leaks, especially at valve outlets, glands, and flange tie-ins, paying particular attention to areas which have recently undergone maintenance or replacement. If no gross leaks are found, the system is slowly brought up to operating pressure and temperature. The expansion of equipment at high temperature generally serves to "tighten up" any pinpoint leaks which may exist, and a leak-free condition is said to exist when, at operating pressure, no more than 145 cubic feet per hour (3500/24 hr) of gas is lost from the system. If any leaks are found, the system is depressurized and the appropriate maintenance work is done.

Voluntary Shutdown

At the scheduled run shutdown time, a voluntary shutdown is initiated. This is done by first venting all process gases to a flare stack and then purging the system twice with inert gas, then allowing the system to cool down for 24 to 48 hours. When the reactor contents are cool, flanges on the gasifier are opened to allow quenched residual solids to fall into large aluminum tote bins. The solids are disposed of as landfill. Voluntary shutdown is essentially a safe procedure, the only safety hazard being incomplete purging of process gas prior to cracking the flanges. This is avoided by having two complete purges before cool-down, and by avoiding difficult to purge S-bends and blind piping in the original design.

Emergency Shutdown

Emergency shutdown should be initiated in the case of a fire, as noted before, or in case of equipment failure, such as faulty refractory lining causing a vessel shell to overheat. The latter is signaled by a discoloration in a heat-sensitive paint on the vessel or piping. Such an occurrence should be observed at routine hourly inspection by the operators during process runs. If a hot spot is noted, a stream of dry, superheated steam should be immediately directed on the spot to keep it cool. If the spot continues to rise in temperature, emergency shutdown should be initiated. The coal feed should be stopped immediately, opening all valves to headers terminating at flare stacks. Inert gas purging through the system should be initiated to halt combustion.

It is essential in case of emergency shutdown to confirm that all valves are in fact open and that no pockets of hot, high-pressure gases remain in the system. This is done by operator inspection of all valves and pressure gauges. Furthermore, after such shutdown, all vessels and pipes should be tested for wall thickness and freedom from cracks by means of an ultrasonic wall thickness gauge applied to the outside of the vessel or pipe.

MAINTENANCE

Safety recommendations for maintenance procedures have the common requirement that any work be fully coordinated via clear communication between operations staff and the various maintenance teams. An effective means of accomplishing such communication is by requiring that a "safe work permit" be issued by the shift supervisor before any maintenance work is done. In the process of approving the work permit, the supervisor must determine which valves and electrical equipment must be locked to assure the safety of the system requiring maintenance. Before work is begun, the valves and electrical equipment thus identified are locked in the appropriate positions and tagged to indicate the nature of the work being done, and to warn other workers not to tamper with them. A thorough description of the CO_2 Acceptor work permit, lock-out, and tag-out procedure can be found in the "Operational Safety Practices for Coal Gasification Plant, Rapid City, South Dakota" (Stearns-Roger 1972).

When vessel entry is required, the same permit procedure should be followed, with the additional stipulation that thorough tests for toxic gases, explosive conditions, and oxygen concentration be carried out prior to entry. Supplied air, continuous flow, full-face piece breathing apparatus should be used if there is any possibility of hazard from toxic gases or insufficient oxygen. If an explosive mixture is found, the vessel must be repurged with inert gas and the above tests must be repeated.

Similar tests to those already described, with the exception of oxygen concentration tests, must be performed on any piping that is to be opened for work.

All maintenance procedures that include welding, cutting, or grinding to be done in the plant area should be approved beforehand by the issuance of a "hot work permit." This permit should not be issued until the shift supervisor has ascertained, by means of inspection and combustible gas tests, that the work area is free of combustible material and that the area is shielded in such a way that sparks from the operation do not fall to floors below or fly to another, uninspected area. The permit should be good only for the time and job specified by the shift supervisor on the permit form. If work must continue into another shift, the new supervisor should approve the work permit for that shift.

FIRE

Fire hazards are not unique to the pilot plant. The unique aspect of the coal gasification pilot plant is that all process units are linked without surge. If one section requires emergency shutdown, then all sections must go into emergency shutdown procedures.

The emergency shutdown procedure has already been described. Fire fighting follows normal procedures used in any refinery or gas transmission station. However, three points must be emphasized:

- A combustible process material will pass through the break before igniting. As long as there is pressure in the vessel, no air can get into it. Some pressure should be maintained in the vessel until it is completely purged of combustible material and the fire dies out.
- A fire in a high-pressure vessel should not be extinguished. The combustible gases will continue to spew from the vessel, creating an explosion hazard. Instead, the vessel contents should be dumped to the flare, as already described, and inert gas purging should be initiated simultaneously.
- While structures should be kept cool during a fire, it could be dangerous to wet down or to otherwise excessively cool hot reaction vessels. This sudden cooling could cause excessive stresses to develop and could either seriously weaken the vessel or cause additional leaks to develop.

Existing OSHA regulations are not specifically applicable to coal gasification pilot plants, especially with respect to the potential hazards that exist in them. Documents that are more directly applicable to these conditions include:

- American Standard Codes for Pressure Piping, ASA B31.1-1955 and B31.8-1958. The American Society of Mechanical Engineers, New York
- The ASME Boiler and Pressure Vessel Code - Section 8, Unfired Pressure Vessels - 1965, The American Society of Mechanical Engineers, New York
- Battelle-Northwest Pressure Systems Manual, BNWL-MA-21
- Hanford Engineering Standards
  - HWS-10000 - Architectural-Civil Standards
  - HWS-10001 - Mechanical Standards
  - HWS-10002 - Electrical Standards
  - HWS-10003 - Guides, Vol. 1
  - HWS-10003 - Guides, Vol. 2
  - HWS-10004 - Welding Standards
  - HWS-10005 - Instrument Standards
  - HWS-10006 - Standard Design Criteria
  - HWS-10007 - Protective Clothing Standards
- National Fire Codes, The National Fire Protection Association, Boston (1965)
  - Volume 1, Flammable Liquids
  - Volume 2, Gases
  - Volume 3, Combustible Solids, Dust, and Explosives
  - Volume 4, Building Construction and Facilities
  - Volume 5, Electrical (The National Electrical Code)
  - Volume 6, Sprinklers, Fire Pumps, and Water Tanks
  - Volume 7, Alarm and Special Extinguishing Systems
  - Volume 8, Portable and Manual Fire Control Equipment
  - Volume 9, Occupancy Standards and Process Hazards
  - Volume 10, Transportation

- Safety Code for Cranes, Derricks, and Hoists - 1943, Reaffirmed 1952, ASA B30.2, United States of American Standards Institute
- Safety Code for Elevators, Dumbwaiters, and Moving Walks - 1965, ASA A17.1, United States of American Standards Institute
- Uniform Building Code, Vol. 1, International Conference of Building Officials, Pasadena, California (1964)

RECOMMENDATIONS FOR FURTHER RESEARCH

During the development of this document it has become increasingly obvious that there is very little hard information on the subject of occupational health in coal gasification plants. Further development of reasonable and real criteria for the protection of the workers in this new industry can only be accomplished when there is an honest understanding of the true nature of the problem. Until then, recommendations such as the ones that appear in this document must be considered preliminary.

This section summarizes overall research needs as well as important areas for future research in process, process equipment, health effects, monitoring and analytical procedures, industrial hygiene, and safety. The recommendations should generate more thoughts on the subject.

INDUSTRIAL HYGIENE SURVEY

Comprehensive, reliable industrial hygiene surveys of breathing zone and ambient air concentrations of potentially hazardous materials in pilot plants are sorely lacking. Precise standards cannot be developed before data are available on which to base them. The following information gathering tasks must be performed for each work station in each pilot plant:

- Description of operation
- Determination of number of workers exposed
- Determination of the nature of employee exposures to potentially toxic agents
- Description of these exposures
- Correlation of the extent of worker exposures to materials in process streams
- Description of ventilation systems and their efficacy
- Documentation of work practices instituted to reduce worker exposure
- Documentation of existing conditions
- Documentation of past and present industrial hygiene practices

The NIOSH Appalachian Laboratory for Occupational Safety and Health is engaged in a study of ambient air concentrations at coal gasification facilities and will determine the information listed above.

Accurate information on specific toxic agents and on classes of toxicants that might be expected in the workplace air of a coal gasification facility is of equal importance to the industrial hygienist. Initially, qualitative analysis of the workplace air should be performed. (Qualitative sampling of the HYGAS facility has been completed.) Quantitative sampling and analysis will be completed at a later date. More specific quantitative monitoring should be done to determine levels of hazardous materials in all work areas of the pilot plant. Procedures that are recommended for the qualitative analysis include the following:

- High-volume area sampling and analysis aimed at determining classes of compounds
- Personal monitoring
- Strict correlation of samples with work stations and environmental monitoring protocols
- Toxicological testing of collected materials
- Overview analysis of plant
- Validation of indicator contaminants to measure indices of exposure

Once potentially hazardous agents in the various work stations have been identified, extensive quantitative sampling should be done to obtain information on worker exposures. During this in-depth industrial hygiene survey the following tasks should be performed:

- Determination of 8-hour time-weighted average and peak concentrations of potentially harmful agents
- Collection of area samples where high concentrations are suspected
- Collection of enough samples to provide statistically valid data

INFORMATION TRANSFER

A primary reason for construction of a pilot plant is to perform experiments on a large scale so that operating problems can be evaluated and corrected. Data on process and major problems are transmitted on a routine basis. In addition routine maintenance problems dealing with pumps, valves, flanges, cavitation, material, etc., are solved at the pilot plant. While they may be solved routinely in one plant, they may present difficulty in another. Because the problems are not always major and because they are not concerned with process data, information concerning their solution can be lost. There should be a mechanism for transmitting this information to management at other pilot operations and to the designers of the demonstration and commercial plants. ERDA could be the centralized data collection center, with information disseminated to each of the interested groups on a routine regular basis. Alternately, a private contractor could also serve in this capacity.

PROCESS AREAS

(a) The actual range of pretreater effluents, especially of the oils and tars, should be defined. The gaseous effluents in the 800°F (427°C) range may be more hazardous than those from the gasifier. It is probable that the off-gas may contain tars boiling above 800°F (427°C) because of either vapor pressures within the pretreater or polymerization reactions of the components.

(b) A study of the thermal oxidation process area should be undertaken to verify that complete oxidation of polynuclear aromatic hydrocarbons has been effected.

(c) The formation of oxides of nitrogen in flares, furnaces, and oxidizers is probable in the combustion area. If an amine process is used in acid gas removal, ambient concentrations of amines may be present. Information should be developed to determine the probability that the oxides of nitrogen will react with the amines to form nitrosamines.

(d) Knowledge of the constituents of the gas stream at each point in the process is crucial in identifying the compounds to which employees may be exposed. The true distribution of sulfur and nitrogen decomposition products, for example, should be determined. At this time, estimation of the total distribution is based primarily on reactions determined by calculations. (Appendix E presents material flows for the Synthane process. Concentrations of potentially carcinogenic oils and tars have been estimated on the basis of vapor pressure alone.)

(e) The fate of trace metals in the coal has not been accurately described. More explicit information on the subject should be gathered through more in-depth analysis of the gas stream.

(f) Detailed study is needed to determine the various components present in the gasifier for each process, and the affect of the temperature gradient on the condensation of the gasifier component products. What is the effect of shutdown on the deposition of carcinogenic products on surfaces that will be contacted by maintenance and/or production workers?

(g) Study is needed to determine the volatilities of trace elements, especially those of a toxic nature, after the method of Attari. The quantitative analysis of toxic elements in each of the process streams is desirable so that worker exposure may be determined.

(h) Existing data for the CO_2 Acceptor (personal communication, Oct. 27, 1976, with D. McCoy, c/o CO_2 Acceptor Pilot Plant, Rapid City, South Dakota), personal observations at the Synthetic Fuels Pilot Plant, and Synthane bench scale data (Massey et al. 1975) indicate that deep-bed injection produces less tar, phenol, cyanide, and thiocyanate than free-fall injection of the coal. Research is needed to determine the optimum economical operating conditions to limit these undesirable products.

(i) It is assumed that the coked or ashed solids from the reactor are essentially inert. Study is required to determine the real hazard classification of these solids (i.e., are they dust hazards, carcinogenic, toxic, neutral, etc.).

(j) Activated carbon is used as an adsorbent in many chemical processes. There is research needed to determine whether char can act as an adsorbent for oil and trace metals.

(k) There is the possibility of iron carbonyl formation as a result of the reaction between carbon monoxide and carbon steel pipe at high pressures and low temperatures. Research should be undertaken to determine the extent of this reaction. The quantity of iron carbonyl formed should be determined, as well as its effect on the methanator catalyst, and the possibility for worker exposure.

(l) Under certain operating conditions or temperatures nickel carbonyl may be formed. The maintenance of temperatures above 500°F (260°C) while the synthesis gas is in contact with the catalyst will avoid this problem. However, in the event of an upset in the operating parameters or a "crash shutdown" of part of the process, the operating condition may no longer be safe. There is a need to determine the conditions under which nickel carbonyl is formed at the methanator. If it is formed, what is the potential for worker exposure and environmental damage?

HEALTH EFFECTS

(a) The relative toxicity of aromatic hydrocarbons condensed on the exterior surfaces of equipment and structures should be determined. These hydrocarbons are considered a source of contamination, but as yet little is known on the subject. (Studies will be conducted in each of three pilot plants to determine the presence of polynuclear aromatic [PNA] hydrocarbon compounds. Ultraviolet [UV] detection of settled PNA compounds should be employed in this study.)

(b) Rapid tests should be developed to determine the relative hazard (toxicity, mutagenicity, and/or carcinogenicity) of whole process streams. When fugitive emissions occur, whatever their cause, employees are exposed to the total stream of emissions, not single compounds or fractions. The total process stream contains both inhibitors and cocarcinogens. The entire toxic effect of the emissions may be tremendously enhanced (or diminished) by the presence of those compounds. Even the test material for the Ames test, as developed by Dr. J. Epler for testing coal conversion effluents, must be fractionated into 14 separate parts (Guerin 1976).

A program of surveillance for occupational teratogenicity, which is now feasible, should also be developed. (NIOSH research in this area is ongoing and the results are expected in the summer of 1978.)

(c) Fifty-one cases of skin lesions reported by Sexton offer an opportunity for follow-up of medical records to look for the association observed by Holmes et al. (1970) in men with scrotal epithelioma, i.e., enhanced incidence of malignancies of the respiratory and upper disgestive tracts. It is recommended that this be done and that consideration be given to follow-up of other workers who were at the Union Carbide plant in Institute, West Virginia.

(d) The Pittsburgh Energy Research Center has a 25-year history of work on coal treatment and conversion without a reported case of cancer. (Other coal oriented research facilities have made similar statements.) A follow-up of medical records for each of the workers who have left the center should be instituted to determine the incidence of any type of cancer and, where applicable, cause of death. There are other fertile areas for retrospective epidemiological studies of workers in facilities studying coal conversion. These should be identified and followed up as rapidly as possible.

(e) Medical histories, in conjunction with work histories, can benefit others as well as the workers examined. These records can provide the data base for prospective and retrospective epidemiologic studies of great potential value in determining the health hazards of coal gasification. It is recommended that steps be taken to maximize the usefulness of future records and the availability of past and future records. Such steps would include standardization of a basic testing protocol and of record formats, and perhaps establishment of a central depository for records from terminated projects. It is recommended that no test be introduced specifically for epidemiologic use.

(f) Research is needed on the interaction effects of chemical carcinogens and physical agents, such as heat, ionizing radiation, noise, etc., to determine the potential for increase or decrease of workers' risk.

Studies are under way at the Biomedical Science Laboratories in Cincinnati, Ohio, to determine interaction effects between heat and benzo[*a*]pyrene. The estimated available date for the report is early 1979.

While the biomedical studies will be illuminating, further work of whole process streams is needed.

MONITORING AND ANALYTICAL PROCEDURES

(a) A real-time monitor for polycyclical aromatic hydrocarbon (PAH) compounds or an indicator such as B*a*P is desirable. A possible approach is diagramed in Figure 23.

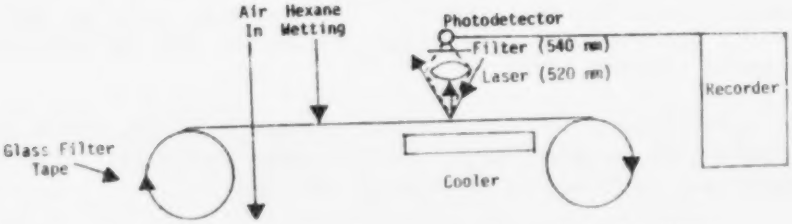

Figure 23. Schematic for low-temperature, laser-excited B*a*P monitor.

The device uses the principle of low-temperature, laser-excited fluorescence. Both discrimination of B*a*P and signal intensity are increased severalfold through the temperature dependence of the Boltzmann distribution. The lowest energy levels are populated at the expense of the higher energy levels as the temperature approaches zero.

For more conventional monitoring, areas of further investigation include problems associated with collection, storage, and analysis of polycyclic aromatic hydrocarbons.

Jones et al. (1975) described an efficient sampling system that increased collection efficiency of PAH compounds as much as 10 times over standard sampling techniques. Adaptability of this method to personal sampling devices for BSFTPM should be explored.

(b) Research must be done on collected particulate matter containing PAH compounds to determine sample losses due to vapor pressure. Perhaps the ideal experimental approach would be to generate a defined PAH aerosol and then collect it on standard sampling media such as the following:

- Particulate filter from HIVOL
- Silver membrane filter
- Cold trap
- Combination of above

This could be repeated with various pure PAHs, mixtures of PAHs, particulates coated wtih PAHs, oily particulates coated with PAHs, etc., to resolve the severity of the problem of sample loss due to vapor pressure and to facilitate the development of improved collection techniques.

(c) Alternatives to benzene soluble fraction of total particulate matter as the measure of biologically active carcinogenic material should be explored. The Standard for Exposure to Coke Oven Emissions (Federal Register 1976a) addresses several established alternative analytical techniques. Perhaps a process involving selective solvation of collected particulate matter followed by a total fluorescence (luminescence) scan could be developed to fill this need. Such a research instrument should be superior to present methods based on benzene solubles.

When monitoring for a specific component in the collected PAH is being done, purity of reference material is crucial. In the fluorescence monitor just discussed, for example, care must be taken to ensure that the reference B*a*P material is B*a*P and not a mixture of B*a*P, B*e*P, and other PAHs with closely related physical properties. The feasibility of high-pressure liquid chromatography followed by multipass automatic zone refining should be studied as a means of preparing high-purity reference samples of B*a*P. Bulk electronic conductance could be used to monitor final purity, as conductance will plateau at a final purity not easily verified by any routine analytical chemical or instrumental method. The stability of the B*a*P material during storage must also be demonstrated.

A feasibility determination should also be made for continuous semiautomatic monitoring with remote readout for particulates using some of the newer glass monitors.

(d) Finally, analytical work should be done on the coal fines, chars, ash, and other solid effluents from the coal gasification processes. These should be examined for the presence of soluble aromatic hydrocarbons and leachable trace elements.

It has generally been thought that the solid effluents from coal conversion processes are inert. However, in a number of instances, these solids are contacted with water recycled from the wastewater pond, or with water recycled internally such as in the coal grinding gas scrubber, and the pretreater and gasifier off-gas venturi scrubbers. These solids are reasonably porous and may absorb or concentrate phenols, tars, or trace elements from the water.

INDUSTRIAL HYGIENE

(a) Protective clothing for the coal gasification worker is necessary. While the type of clothing has been described and suggested in the chapter on health protection, however, no information is available defining material in that clothing. Research is required on the following:

- Coveralls
- Gloves—for various purposes
- Shoes—particularly on the best type of sole
- Underclothing

(a) Barrier creams seem to be controversial and more information on their effectiveness must be gathered. A useful barrier cream should be developed. A standard test for these creams should be devised and used to make publishable comparisons. The Pittsburgh Energy Research Center (PERC) has conducted a preliminary internal survey on barrier creams and has found varying degrees of effectiveness. They have found that effectiveness is dependent upon the conscientiousness of the individuals involved. Research is needed to develop an effective long lasting barrier cream. A standard test for these creams should be determined and published as part of the manufacturing specifications.

(b) The effectiveness of available cleansing materials for removal of tars from the skin should also be investigated. More effective materials are needed.

(c) The permissible concentration of PAH materials in the cleaning fluid or wash water from the plant laundry facilities should be defined. It is possible that in large gasification plants the percentages of this PAH material could be high.

(d) A cleaning agent should be made available to remove oils and tars from equipment and surrounding structures and from tools used on tarred surfaces. Effective means for disposing of this material should also be developed.

(e) An effective personnel monitoring device should be devised for use in areas where considerable coal-derived hydrocarbons could be present.

(f) The effectiveness of UV light in detecting skin contamination should be thoroughly demonstrated. At the same time the possibility of damage due to the use of UV light for surveillance should be examined. Alternative procedures for contamination detection should also be investigated.

(g) Research is needed to determine the effectiveness of a sputum cytology program in helping to protect the exposed workers.

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Appendix A. Possible constituents of gasifier off-gas.

As has been mentioned several times in this report, there are no good analytical data characterizing constituents of gasifier off-gas. In the "Research Recommendations" section the need for further analytical work on components of the gas stream has been emphasized. In the absence of analytical data and keeping in mind the fact that off-gases from the different processes will vary we present here a list of products of coal pyrolysis. (Coal pyrolysis is the oxygen-deficient reduction of coal. It is similar to several of the coal gasification processes.) The compounds listed in this appendix are intended only as a first approximation of possible constituents of the gasifier off-gas.

Products of coal pyrolysis represent a myriad of different organic species. Complete analyses of coal tars have, over the years, generated long lists of polycyclic aromatic hydrocarbons (PAHs) and heterocyclic hydrocarbons. This appendix presents several tables that categorize identified coal tar constituents by boiling range. Constituents of coal liquefaction have not been included in the list of coal pyrolysis products because it was determined that different compounds would result from the two procedures.

Table A-1 is a partial list of coal tar constituents compiled from Freudenthal and co-workers (1975), Dailey (1976), and Ensminger (1976). An "x" in the "Present in Gasification" column of this table indicates that the compound has been identified in the process condensate from a bench scale gasification unit (Guerin and Epler 1976) or in the condensate from the MERC unit (Gillmore and Liberatore 1975). In addition, Wynder and Hoffman (1967) and Kornreich (1976) have been used to identify coal tar compounds with known carcinogenic activity. Most of the compounds indicated as carcinogenic have undergone toxicologic testing in animals and have been generally accepted by the scientific community as being primary carcinogens. Examples of cocarcinogenic compounds are also included. Compounds that are under question as to their carcinogenic potential have not been indicated. Insufficient data exist to make a more exhaustive table.

Tables A-2 and A-3 are taken from a Bureau of Mines report (Karr et al. 1961). They list tar acids and tar bases that were identified in low-temperature bituminous coal tar. The fact that a compound is listed in these tables does not mean that it will necessarily be in the gas stream, but rather that it could be in the gas stream. This is some indication of the complexity of the problem.

Table A-1. Possible constituents of gasifier off-gas categorized by boiling range.[a,b,c]

	Present in[d,e] Gasification	Known[f,g] Carcinogen
Boiling Point < 100°C		
Aliphatic Hydrocarbons:		
Amylene		
1,5-Butadiene		
Butylene		
Crotonylene		
Heptane		
Heptene		
Hexane		
Hexene		
Pentane		
Cyclic Hydrocarbons:		
Cyclohexadiene		
Cyclohexane		
Cyclohexene		
Cyclopentadiene		
Aromatic Hydrocarbon:		
Benzene	x	x
Oxygen-containing Compounds:		
Acetaldehyde		
Acetone		
Carbon monoxide	x	
Methyl ethyl ketone		
Nitrogen-containing Compounds:		
Acetonitrile		
Ammonia	x	
Hydrogen cyanide		
Nitrogen oxides		
Sulfur-containing Compounds:		
Carbon disulfide		
Carbonyl sulfide	x	
Diethyl sulfide		
Dimethyl sulfide		
Ethyl mercaptan		
Hydrogen sulfide	x	
Methyl mercaptan		
Sulfur dioxide		
Thiophene		
	Present in Gasification	Known Carcinogen
Boiling Point = 100°C to 150°C		
Aliphatic Hydrocarbon:		
Octane		
Cyclic Hydrocarbons:		
Dimethyl cyclohexane		
Methyl cyclohexane		
Nonaphthene		
Aromatic Hydrocarbons:		
Ethylbenzene		
Styrene		
Toluene	x	
o-Xylene		
m-Xylene		
p-Xylene		
Oxygen-containing Compounds:		
Acetic acid	x	
Propanoic acid	x	
Nitrogen-containing Compounds:		
2,6-Dimethyl pyridine		
2-Methylpyridine		
3-Methylpyridine		
4-Methylpyridine		
Pyridine		
Pyrrole		
Sulfur-containing Compounds:		
3-Methylthiophene	x	
Thioxene	x	

(cont'd)

[a] Adapted from Dailey (1976) and Ensminger (1976).
[b] Adapted from Lebowitz et al. (1975).
[c] Adapted from Freudenthal et al. (1975).
[d] Adapted from Gillmore and Liberatore (1975).
[e] Adapted from Guerin and Epler (1976).
[f] Adapted from Wynder and Hoffman (1967).
[g] Adapted from Kornreich (1976).

Table A-1. (cont'd)

	Present in Gasification	Known Carcinogen
Boiling Point = 150°C to 200°C		
Aliphatic Hydrocarbon:		
Decane		
Cyclic Hydrocarbon:		
Dicyclopentadiene		
Aromatic Hydrocarbons:		
Cymene		
Durene		
o-Ethyltoluene		
m-Ethyltoluene		
p-Ethyltoluene		
Hemellitene		
Hydrindene		
Isodurene		
Isopropylbenzene		
Mesitylene		
n-Propylbenzene		
Pseudocumene		
Polynuclear Aromatic Hydrocarbons:		
2,7-Dimethylindene		
3,6-Dimethylindene		
Indene	x	
Oxygen-containing Compounds:		
n-Butanoic acid	x	
Coumarone		
o-Cresol	x	
Dimethylcoumarone		
n-Pentanoic acid	x	
Phenol	x	cocarcinogen
Nitrogen-containing Compounds:		
Aniline		
Benzonitrile		
Dimethylaniline		
2,3-Dimethylpyridine		
2,4-Dimethylpyridine		
2,5-Dimethylpyridine		
3,4-Dimethylpyridine		
Toluidine		
2,4,5-Trimethylpyridine		
2,4,6-Trimethylpyridine		

	Present in Gasification	Known Carcinogen
Boiling Point = 200°C to 250°C		
Aliphatic Hydrocarbon		
n-Dodecane		cocarcinogen
Polynuclear Aromatic Hydrocarbons:		
Cholanthrene		
Dihydronaphthalene		
4,6-Dimethylindene		
5,7-Dimethylindene		
1-Methylnaphthalene	x	
2-Methylnaphthalene	x	
Naphthalene	x	
Oxygen-containing Compounds:		
Acetophenone		
Benzoic acid		
m-Cresol	x	
p-Cresol	x	
2,2'-Dihydroxydiphenyl		
2,3-Dimethylphenol	x	
2,4-Dimethylphenol		
3,4-Dimethylphenol	x	
3,5-Dimethylphenol	x	
2,6-Dimethylphenol	x	
2,5-Dimethylphenol	x	
Dimethylcoumarone		
Durenol		
o-Ethylphenol	x	
m-Ethylphenol		
p-Ethylphenol		
n-Heptanoic acid	x	
Isopseudocumenol		
3-Methyl-5-ethylphenol		
Nitrogen-containing Compounds:		
Acetamide	x	
Isoquinoline		
2-Methylquinoline		
8-Methylquinoline		
Propionamide	x	
Quinoline		
1,2,3,4-Tetramethylpyridine		

(cont'd)

Table A-1. (cont'd)

	Present in Gasification	Known Carcinogen
Boiling Point = 200°C to 250°C (cont'd)		
Sulfur-containing Compounds:		
Diallylsulfide		
Dimethylbenzothiophene		
Methylbenzothiophene		
2,3-Benzothiophene		
Boiling Point = 250°C to 300°C		
Aromatic Hydrocarbons:		
3,4'-Dimethyldiphenyl		
4,4'-Dimethyldiphenyl		
Diphenyl	x	
2-Methyldiphenyl		
3-Methyldiphenyl		
4-Methyldiphenyl		
Polynuclear Aromatic Hydrocarbons:		
Acenaphthylene	x	
Acenaphthene	x	
1,2-Cyclopentanonaphthalene		
1,2-Dimethylnaphthalene	x	
1,3-Dimethylnaphthalene	x	
1,5-Dimethylnaphthalene	x	
1,6-Dimethylnaphthalene	x	
1,7-Dimethylnaphthalene		
2,6-Dimethylnaphthalene	x	
2,7-Dimethylnaphthalene		
2,3-Dimethylnaphthalene	x	
1-Ethylnaphthalene		
2-Ethylnaphthalene		
Fluorene	x	
Oxygen-containing Compounds:		
Diphenylene oxide		
1-Methyldiphenylene oxide		
1-Naphthofurane		
2-Naphthofurane		
α-Naphthol	x	
β-Naphthol	x	
Resorcinol		
Boiling Point = 250°C to 300°C (cont'd)		
Nitrogen-containing Compounds:		
1,3-Dimethylisoquinoline		
2,8-Dimethylquinoline		
5,8-Dimethylquinoline		
Indole		
2-Methylindole		
3-Methylindole		
4-Methylindole		
5-Methylindole		
7-Methylindole		
1-Methylisoquinoline		
3-Methylisoquinoline		
3-Methylquinoline		
4-Methylquinoline		
5-Methylquinoline		
6-Methylquinoline		
7-Methylquinoline		
1-Naphthonitrile		
Boiling Point > 300°C		
Aliphatic Hydrocarbons:		
n-Heptadecane		
Nonadecane		
Polynuclear Aromatic Hydrocarbons:		
Anthracene		
1,2-Benzanthracene		x
2,3-Benzchrysene		
3,4-Benzfluorene		
Benz[*m*,*n*,*o*]fluoranthene		
2,3-Benzfluoranthene		x
3,4-Benzfluoranthene		
7,8-Benzfluoranthene		x
8,9-Benzfluoranthene		
1,2-Benzfluorene		
2,3-Benzfluorene		
1,2-Benznaphthacene		
1,2-Benzoanthracene		
1,2-Benzpentacene		

(cont'd)

Table A-1. (cont'd)

	Present in Gasification	Known Carcinogen
Boiling Point: > 300°C (cont'd)		
Polynuclear Aromatic Hydrocarbons (cont'd)		
1,12-Benzperylene		
3,4-Benzphenanthrene		x
1,2-Benzpicene		
1,2-Benzpyrene		x
4,5-Benzpyrene		x
Chrysene		x
Coronene		
1,2,3,4-Dibenzanthracene		
1,2,5,6-Dibenzanthracene		x
1,2,7,8-Dibenzanthracene		
1,2,6,7-Dibenzpyrene		x
1,2,7,8-Dibenzpyrene		x
3,4,8,9-Dibenzpyrene		
3,4,9,10-Dibenzpyrene		
3,4,8,9-Dibenztetraphene		
9,10-Dihydroanthracene	x	
5,12-Dihydronaphthacene		
9,10-Dimethylphenanthrene		
2,3-Dimethylanthracene		
2,7-Dimethylanthracene		
3,6-Dimethylphenanthrene		
2,2-Dinaphthyl		
Diphensuccindan		
Fluoranthene	x	cocarcinogen
1-Methylanthracene		
2-Methylanthracene		
9-Methylanthracene		
1-Methylchrysene		x
2-Methylchrysene		x
1-Methylfluorene		
3-Methylfluorene		
9-Methylfluorene		
1-Methylphenanthrene		
2-Methylphenanthrene		
3-Methylphenanthrene		
9-Methylphenanthrene		
1-Methylpyrene		cocarcinogen
3-Methylpyrene		cocarcinogen
4-Methylpyrene		cocarcinogen
Boiling Point: > 300°C (cont'd)		
Polynuclear Aromatic Hydrocarbons (cont'd)		
Naphthacene		
Naphthofluorene		
Naphtho-2',3'-1,2-anthracene		
Perylene		
Phenanthrene	x	
4,5-Phenanthrylene methane		
2,3-*o*-phenylene pyrene		
1-Phenylnaphthalene	x	x
2-Phenylnaphthalene	x	x
2-Phenylphenanthrene		
Picene		
Pyrene		cocarcinogen
1,2,3,4-Tetrahydroanthracene		
1,2,3,4-Tetrahydrofluoranthene		
2,3,6,7-Tetramethylnaphthalene		
1,3,7-Trimethylnaphthalene		
1,3,6-Trimethylnaphthalene		
1,2,8-Trimethylphenanthrene		
Triphenylene		
Truxene		
Oxygen-containing Compounds:		
Benzanthrone		
1,2-Benzdiphenylene oxide		
1,9-Benzoxanthene		
Brazan		
Dibenzocoumarone		
1,8-Dimethylphenylene oxide		
o,*o*'-Diphenol		
5-Diphenyl-γ-pyrone		
Hydroxyanthracenes		
4-Hydroxydiphenyl		
2-Hydroxyfluorene		
9-Hydroxy-4-methylfluorene		
p-Methoxybenzophenone		
Methyl brazans		
2-Methyldiphenylene oxide		
3-Methyldiphenylene oxide		

(cont'd)

Table A-1. (cont'd)

	Present in Gasification	Known Carcinogen
Boiling Point: > 300°C (cont'd)		
Oxygen-containing Compounds (cont'd)		
peri-Naphthoxanthene		
o(β-Naphthyl)phenol		
2-Phenanthrol		
4-Phenanthrol		
1-Phenylbenzanthrone		
p-Phenylphenol		
Tetramethyldiphenol		
Xanthene		
Nitrogen-containing Compounds:		
Acridine		
1-Azacarbazole		
2-Azafluoranthene		
13-Azafluoranthene		
4-Azafluorene		
1-Azapyrene		
1,2-Benzacridine		
3,4-Benzacridine		x
2,3-Benz-1-azacarbazole		
2,3-Benz-4-azafluorene		
1,2-Benzcarbazole		
2,3-Benzcarbazole		
3,4-Benzcarbazole		
2,3-Benzfluorenenitrile		
5,6-Benzquinoline		
7,8-Benzquinoline		
Carbazole		
1,2,5,6-Dibenzacridine		x
1,2,7,8-Dibenzacridine		x
9,10-Dihydroacridine		
Fluorene nitriles		
Hydroacridine		
Indeno[1,2,3-*c*,*d*]pyrene		x
4,5-Iminophenanthrene		
2-Methylacridine		
2-Methyl-5,6-benzquinole		
Boiling Point: > 300°C (cont'd)		
Nitrogen-containing Compounds (cont'd)		
2-Methylcarbazole		
3-Methylcarbazole		
2-Naphthonitrile		
1-Naphthylamine		
2-Naphthylamine		
1-oxo-1,2-dihydro-2-azapyrene		
Phenanthridene		
1,2,3,4-Tetrahydroacridine		
Sulfur-containing Compounds:		
1,2-Benzdiphenylene sulfide		
Benzo[*d*,*e*,*f*]dibenzothiophene		
4,5-Benzthionaphthene		
5,6-Benzthionaphthene		
6,7-Benzthionaphthene		
Benzylthiophene		
Dibenzothiophene		
2,3,5,6-Dibenzthionaphthene		
1,8-Dimethylphenylene sulfide		
Dinaphthothiophene		
Diphenylene sulfide		
Methyldibenzothiophene		
Methylthiophene		
Tetrahydrobenzothiophene		
Naphthobenzothiophene		

Table A-2. Index of individual tar acids from low-temperature bituminous tar based on boiling range.

Compound	Boiling Range, °C[a]
Phenol	182
2-Methylphenol	190.8
2,6-Dimethylphenol	201
4-Methylphenol	202.1
3-Methylphenol	202.2
2-Ethylphenol	207
2,4-Dimethylphenol	210
2,5-Dimethylphenol	210
2-Ethyl-6-methylphenol	212-214
3-Ethylphenol	214
2-Isopropylphenol	214
2-Ethyl-4-methylphenol	216-218
2,3-Dimethylphenol	218
4-Ethylphenol	219
3,5-Dimethylphenol	219.5
2,3,6-Trimethylphenol	220
2-n-Propylphenol	220
4-Ethyl-2-methylphenol	222
2,4,6-Trimethylphenol	222
5-Ethyl-2-methylphenol	223
2-Ethyl-5-methylphenol	224.2
3,4-Dimethylphenol	225
3-Ethyl-2-methylphenol	227
2,4-Dimethyl-6-ethylphenol	227-228
3-n-Propylphenol	228
3-Isopropylphenol	228
2-Isopropyl-3-methylphenol	228.5
2-Isopropyl-4-methylphenol	228-229/763
4-Isopropylphenol	228-229/745
4-Ethyl-3-methylphenol	228-230
2-(Propen-1-yl)phenol	230-231
2,4,5-Trimethylphenol	232
4-n-Propylphenol	232.6
2-Methyl-6-n-propylphenol	233
3-Ethyl-5-methylphenol	233
2,3,5-Trimethylphenol	233

(cont'd)

[a] All temperatures are measured at atmospheric pressure unless followed by a slash (/). The number to the right of the slash is the pressure at which the boiling ranges were obtained, in mm. Figures in parentheses are atmospheric boiling points estimated from reduced pressure data or from boiling-point data of isomers and homologues, in mm.

Table A-2. (cont'd)

Compound	Boiling Range, °C[a]
2-Isopropyl-5-methylphenol	233.5
4-Isopropyl-2-methylphenol	230-235
3-Ethyl-4-methylphenol	234-235
2,3,4-Trimethylphenol	235-237
5-Isopropyl-2-methylphenol	236.8-237.4
4-Isopropyl-3-methylphenol	238
2,3-Dimethyl-6-ethylphenol	(240)166/100
4-Methyl-2-n-propylphenol	(241)121-123/18
3-Isopropyl-5-methylphenol	241
4-Indanol	245/764
Catechol	245
2,3,5,6-Tetramethylphenol	247-248
3,5-Diethylphenol	248
3-Methylcatechol	248
3,4,5-Trimethylphenol	248-249
3,5-Dimethyl-2-ethylphenol	(250)90-93/1
3,4-Dimethyl-6-ethylphenol	(250)
6-Methyl-4-indanol	(250)
7-Methyl-4-indanol	(250)
2,3,4,6-Tetramethylphenol	250
5-Indanol	255
2,6-Di-n-propylphenol	256/764
4-Methylcatechol	258
3,5-Dimethyl-2(propen-1-yl)phenol	(260)
7-Methyl-5-indanol	(260)
2,3,4,5-Tetramethylphenol	260
5,6,7,8-Tetrahydro-1-naphthol	264.5-265/705
2-Ethylresorcinol	(265)
Pentamethylphenol	267
4-Ethylresorcinol	(270)131/15
2-(Cyclopenten-2-yl)phenol	(270)133-135/12
2-(Cyclopenten-1-yl)phenol	(272)
2-Phenylphenol	275
5,6,7,8-Tetrahydro-2-naphthol	275-276
4-Methyl-5,6,7,8-tetrahydro-1-naphthol	(280)
4-Methyl-2-phenylphenol	(280)101-105/2
2-Cyclohexylphenol	282.5-283.5
2-(Cyclopenten-2-yl)-4-methylphenol	(284)105-108/1.3
2-Ethylhydroquinone	(285)
1-Naphthol	288.01
3-Methyl-5,6,7,8-tetrahydro-2-naphthol	(290)
4-Methyl-5,6,7,8-tetrahydro-2-naphthol	(290)
4-(Cyclopenten-1-yl)phenol	(293)
4-(Cyclopenten-2-yl)phenol	(293)114-117/1.5
2-Naphthol	294.85

(cont'd)

Table A-2. (cont'd)

Compound	Boiling Range, °C[a]
2-Methyl-1-naphthol	(295)
4-Cyclohexylphenol	293.5-295.5/752
4-Methyl-1-naphthol	(298)177-179/25
1 Methyl-2-naphthol	(300)
1,4-Dimethyl-5,6,7,8-tetrahydro-2-naphthol	(305)
5-Methyl-2-naphthol	(305)
3,4-Dimethyl-1-naphthol	(315)205-210/15
4-Phenylphenol	319
7-Ethyl-4-methyl-1-naphthol	(320)
3-Phenylphenol	325
5-Acenaphthenol	(332)221/40
4-Acenaphthenol	(338)
1-Fluorenol	(345)
2-Fluorenol	340-350
3-Fluorenol	(350)
8-Methyl-2-fluorenol	(355)

Table A-3. Index of individual tar bases from low-temperature bituminous tar (based on boiling range).

Compound	Boiling Range, °C[a]
Pyridine	115.4
2-Methylpyridine	129.42
2,6-Dimethylpyridine	144.05
3-Methylpyridine	144.14
4-Methylpyridine	145.0
2-Ethylpyridine	148.6
2,5-Dimethylpyridine	157.01
2,4-Dimethylpyridine	158.40
2-Isopropylpyridine	158.9
2,3-Dimethylpyridine	161.16
2-Ethyl-6-methylpyridine	160-161.5
3-Ethylpyridine	162-165/762
2,4,5-Trimethylpyridine	165-168
4-Ethylpyridine	169.6-170/750
3,5-Dimethylpyridine	171.91
2,4,6-Trimethylpyridine	171-172
4-Isopropylpyridine	173
5-Ethyl-2-methylpyridine	174-176
2,3,6-Trimethylpyridine	176-178/759
3-Isopropylpyridine	177-178
3,4-Dimethylpyridine	179.13
4-Ethyl-2-methylpyridine	179-180
2,4-Dimethyl-6-ethylpyridine	181-182
2,3,5-Trimethylpyridine	182-183/739
Aniline	183.93
2,6-Dimethyl-4-ethylpyridine	186
2,4-Diethylpyridine	187-188
2,3,4-Trimethylpyridine	192-193
N,N-Dimethylaniline	192.5-193.5
3-Ethyl-4-Methylpyridine	195-196/753
N-Methylanine	196.1
2,3,5,6-Tetramethylpyridine	197-198
2,3-Cyclopentenopyridine	199.5
2-Methylaniline	200.3
4-Methylaniline	200.55
2,3,4,6-Tetramethylpyridine	203/750
3-Methylaniline	203.34

(cont'd)

[a] All temperatures are measured at atmospheric pressure unless followed by a slash (/). The number to the right of the slash is the pressure at which the boiling ranges were obtained, in mm. Figures in parentheses are atmospheric boiling points estimated from reduced pressure data or from boiling-point data of isomers and homologues, in mm.

Table A-3. (cont'd)

Compound	Boiling Range, °C[a]
N-Methyl-3-methylaniline	206-207
N-Methyl-2-methylaniline	207-208
N-Methyl-4-methylaniline	209-211/761
2,5-Dimethylaniline	213.5
2,6-Dimethylaniline	214/739
2-Ethylaniline	215-216/769
2,4-Dimethylaniline	215.8-216.0/728
3,5-Dimethylaniline	220-221
5,6,7,8-Tetrahydroquinoline	222.2
3,4-Dimethylaniline	226
Quinoline	237.1
2-Methylquinoline	245.8
8-Methylquinoline	247.3-248/751.3
2,8-Dimethylquinoline	252
3-Methylquinoline	252/735
7-Methylquinoline	251.5252.5
5-Methylquinoline	253-255/735
6-Methylquinoline	257.4-258/745
2,3-Dimethylquinoline	261/730
4-Methylquinoline	264.2
2,4-Dimethylquinoline	264-265
2,7-Dimethylquinoline	264-265
2,6-Dimethylquinoline	266-267
2,6,8-Trimethylquinoline	267.4/746
2-Phenylpyridine	268-269
3-Phenylpyridine	269-270/749
2,5,8-Trimethylquinoline	(273)143-145/15
4,6-Dimethylquinoline	273-274
4-Phenylpyridine	274-275
2,4,8-Trimethylquinoline	275.8/740
2,7,8-Trimethylquinoline	276.1/740
2,3,8-Trimethylquinoline	280/747
2,4,7-Trimethylquinoline	280-281
2,5,7-Trimethylquinoline	286.6/746
2,4,6-Trimethylquinoline	287/758
2-Naphthylamine	294
2,4,7,8-Tetramethylquinoline	295.5/742
1-Naphthylamine	300.8
2,4,5,8-Tetramethylquinoline	(310)168-172/12
N-Benzyl-2-methylaniline	(310)176/10
N-Benzyl-3-methylaniline	312
N-Benzyl-4-methylaniline	312-313
7,8-Benzoquinoline	335
6,7-Benzoquinoline	(345)200-205/14
2,3-Benzoquinoline	345-346

(cont'd)

Table A-3. (cont'd)

Compound	Boiling Range, °C[a]
3,4-Benzoquinoline	349/769
5,6-Benzoquinoline	350/721
2,4-Dimethylbenzo(*h*)quinoline	355
1,3-Dimethylbenzol(*f*)quinoline	(358)240/35
9-Methylacridine	359-360/740
2-Methylbenzo(*g*)quinoline	(360)
4-Methylbenzo(*g*)quinoline	(360)
2,3-Dimethylbenzo(*f*)quinoline	(360)
2,4-Dimethylbenzo(*g*)quinoline	(370)
3,4-Dimethylbenzo(*g*)quinoline	(370)

Appendix B. Standards for materials known to be present or possibly present in coal gasification plants.

OSHA standards limiting the concentration of some potentially toxic contaminants in the workplace air have been established under the OSHA Act of 1970. Many of these standards will pertain to coal gasification plants. This appendix presents two tables of the OSHA standards. The first includes names and locations of compounds anticipated in a gasification facility. The second table is a list of compounds for which standards have been adopted and which may be found at some point in a coal gasification plant. These lists are not intended as a comprehensive list of all hazardous compounds, for they cover only material for which there is an OSHA standard. These standards may be found in Federal Register 1976b. Shown in parentheses are the currently available recommended standards from NIOSH Criteria Documents as referenced in the table.

Table 8-1. Standards for materials known to be present in coal gasification plants.[a]

Compound	TWA,[b] ppm	TWA[b] mg/m^3	Acceptable ceiling concentration	Where found
Acetic acid	10	25		Gas stream
Acetone	1000	2400		Laboratory
Ammonia	50	35	50[d]	Gas stream
Aniline-skin	5	19		
Antimony		0.5		Trace element in coal
Arsenic		0.5	(.002 mg/m^3)[e]	Trace element in coal
Benzene	10(1)[f]	-	25(5 ppm)[f]	Gas stream, laboratory
Beryllium		0.002(0.002)[g]	005 mg/m^3	Trace element in coal
1,3-Butadiene	1000	2200		Gas stream
Cadmium fume dust		0.1 0.2(.04)[h]	3 mg/m^3 0.6 mg/m^3(0.2 mg/m^3)[h]	Trace element in coal
Carbon dioxide	5000(10,000)[i]	9000(18,000)[i]	(30000 ppm)[f]	Gas stream
Carbon disulfide	20(1)[j]		30 ppm (10 ppm)[j]	Gas stream
Carbon monoxide	50(35)[k]	55	(200 ppm)[k]	Gas stream
Carbon tetrachloride	10	1	25 ppm	Laboratory
Chromium, soluble salts		0.5 (0.025)[l]	(0.05 mg/m^3)[l]	
Metal, insoluble salts		1		Trace element in coal
Coal dust (<5% SiO_2)		2.4		Coal preparation areas
(>5% SiO_2)		0.10		
Coal tar pitch volatiles		0.2		Gas stream
Cresol-skin	5	22		Gas stream
Ethyl mercaptan		-	10 ppm	Gas stream
Hydrogen chloride		-	5 ppm	Stream
Hydrogen sulfide		-	20 ppm (10 ppm)[m]	Gas stream
Lead and inorganic lead compounds		0.2(0.10)[n]		Trace element in coal
Manganese		-	5 mg/m^3	Trace element in coal
Mercury		0.1(0.05)[o]		Trace element in coal
Methyl ethyl ketone	200	590		Laboratory
Methyl mercaptan		-	10 ppm	Gas stream
Naphtha (coal tar)	100	400		Gas stream
Napthalene	10	50		Gas stream
Nickel carbonyl	0.001	0.007		Methanation areas
Nickel metal and soluble compounds (as Ni)		1		Trace element in coal
Phenol-skin	5	19(20)[p]	(60 mg/m^3)[p]	Gas and effluent stream
Propane	1000	1800		Gas stream
Pyridine	5	15		Gas stream
Selenium compounds		0.2		Trace element in coal
Silica (respirable) (total dust)		0.10(0.05)[q] 0.30		
Styrene	100			
Sulfur dioxide	5(2)[r]	13		Thermal oxidizer
Toluene	200(100)[s]			Slurry oil, gas stream
Vanadium V_2O_5 dust V_2O_5 fume		(1)[t]	(0.05 mg/mg^3)[t] 0.5 mg/m^3 0.1 mg/m^3	Trace element in coal
Xylene	100(100)[u]	435		Gas stream

[a] Federal Register 1976b. Skin after certain compounds indicates that there is the possibility for exposure via a cutaneous route.

[b] Time-weighted average. Numbers in parentheses indicate NIOSH recommended standards.

[c] Coal tar pitch volatiles, as measured by the benzene-soluble fraction of particulate matter, includes such polycyclic aromatic hydrocarbons as anthracene, benzo[α]pyrene, phenanthrene, acridine, crysene, and pyrene.

[d] National Institute for Occupational Safety and Health (1974a).

[e] National Institute for Occupational Safety and Health (1975b).

[f] National Institute for Occupational Safety and Health (1976a).

[g] National Institute for Occupational Safety and Health (1977[illegible]).

[h] National Institute for Occupational Safety and Health (19[illegible]).

[i] National Institute for Occupational Safety and Health (1976c).

[j] National Institute for Occupational Safety and Health (1977a).

[k] National Institute for Occupational Safety and Health (1972b).

[l] National Institute for Occupational Safety and Health (1975a).

[m] National Institute for Occupational Safety and Health (1977b).

[n] National Institute for Occupational Safety and Health (1972b).

[o] National Institute for Occupational Safety and Health (1973b).

[p] National Institute for Occupational Safety and Health (1976g).

[q] National Institute for Occupational Safety and Health (1974a).

[r] National Institute for Occupational Safety and Health (1974b).

[s] National Institute for Occupational Safety and Health (1973c).

[t] National Institute for Occupational Safety and Health (1977e).

[u] National Institute for Occupational Safety and Health (1975c).

Table B-2. Standards for materials possibly present in coal gasification plants.

Compound	ppm	mg/m^3
Butyl mercaptan	10	35
Calcium arsenate		1(0.002)[a]
Cyclohexane	300	1050
Cyclohexanol	50	200
Cyclohexene	300	1015
Cyclopentadiene	75	200
Dimethylamine	10	18
Dimethylsulfate - skin	1	5
Dinitrobenzene - skin		1
Dinitro-*o*-cresol - skin		0.2
Dinitrotoluene - skin		1.5
Diphenyl	0.2	1
Ethanol	1000	1900
Ethanolamine	3	6
2-Ethoxyethanol - skin	200	740
Ethyl acetate	400	1400
Ethylamine	10	18
Ethyl benzene	100	435
n-Heptane	500	2000
n-Hexane	500	1800
Isobutyl acetate	150	700
Methyl acetate	200	610
Methyl alcohol	200(200)[b]	260
Methylamine	10	12
Nitrobenzene - skin	1	5
Nitrogen dioxide	5 (1)[c]	9
Octane	500	2350
Oil mist, mineral		5
Pentane	1000	2950
Petroleum distillates	500	2000
Phosphorus compounds		0.1-3
Picric acid - skin		0.1
n-Propyl acetate	200	840
Propyl alcohol	200	500
Sodium hydroxide		2 (2)[d]
Tellurium		0.1

[a] National Institute for Occupational Safety and Health (1975b).
[b] National Institute for Occupational Safety and Health (1976e).
[c] National Institute for Occupational Safety and Health (1976f).
[d] National Institute for Occupational Safety and Health (1976h).

Appendix C. Monitoring equipment.

Quick response continuous monitors are important for measuring levels of carbon monoxide (CO) and hydrogen sulfide (H_2S) in the ambient air and in the vicinity of potential leaks. The measurement of these compounds may give an indication of the concentration of carcinogenic material in the workplace air (see section on monitoring worker's environment).

Tables C-1 and C-2 list some commercially available instruments that may have applications in the gasification plant environment.

Table C-1. CO monitors.

Manufacturer	Model	Principle of Operation	Sensitivity, ppm
Andros, Inc.	7000	Fluorescence NDIR[a]	0.2
Analytical Instrument Development, Inc.	511-14	GC/FID[b]	0.5
Bachrach Instrument Co.	US400L	Hg Substitution-UV Absorption	0.05
Beckman Instruments, Inc.	866	NDIR[a]	1
Beckman Instruments, Inc.	6800	GC/FID[b]	0.01
Byron Instruments, Inc.	233A	GC/FID[b]	0.01
Calibrated Instruments, Inc.	SL/LC	NDIR[a]	ND
Devco Engineering, Inc.	Series 10 APM,1000	Catalytic Oxidation	0.5
Energetics Sciences, Inc.	Ecolyzer	Electrochemical	0.25
Enviro Metrics, Inc.		Electrochemical cell	0.1
Hewlett-Packard	5831	GC/Thermal Conductivity	10
Horiba	APMA-10	NDIR[a]	0.5
Interscan Corp.	1140 Series	Electrochemical Voltammetric	1
Matheson Gas Products	803 Series	Catalytic Oxidation	1
Mine Safety Appliances	D	Catalytic Oxidation	5
Mine Safety Appliances	70	Thermal Conductivity	1
Mine Safety Appliances	202	NDIR[a]	1
Philips Electronic Instruments	9775	Amperometric	0.03
Wilks	Miran	DIR[c]	0.5

NDIR = Nondispersive infrared spectrometer.
GC/FID = Gas chromatograph with flame ionization detection.
DIR = Dispersive infrared.

Table C-2. H_2S monitors.

Manufacturer	Model	Method of Operation	Sensitivity, ppm
Analytical Instrument Development	511-19	GC/FPD[a]	.03
Barton ITT	246,400, 406	Amperometric	0.03
Bendix/Process Instruments Division	8770	GC/FPD[a]	0.001
Canadian Research Institute	HS-2	Nondispersive UV and Visible Absorption	ND
Ecology Board	300	Voltammetric	2
E.I. du Pont de Nemours and Co.	400	Nondispersive UV and Visible Absorption	2
Energetics Sciences, Inc.	Ecolyzer	Electrochemical	0.1
Hewlett-Packard	5830	GC/FPD[a]	0.001
IBC Celesco	NS-300	Voltammetric	1
International Ecology Systems	A102S	Amperometric	0.002
Interscan Corp.	1170 Series	Electrochemical Voltammetric	0.1
Meloy Labs, Inc.	SA Series	FPD[b]	0.0005
Monitor Labs.	8450	FPD[b]	0.001
Philips Electronic Instruments	PW9700	Amperometric	0.001
Technicon Industrial Systems	Air Monitor IV	Colorimetric-Methylene Blue	0.002
Thermo Electron Corp.	43/340	Pulsed Fluorescence	0.002
Tracor	270H	GC/FPD[a]	.001
Varian Aerograph	1490	GC/FPD[a]	.01

[a] GC/FPD = Gas Chromatograph attached to flame photometric detector.
[b] FPD = Flame photometric detector.

Appendix D. Recommended method[a] for analysis of benzene soluble fraction total particulate matter (BSFTPM).

SAMPLING

Full-shift (8-hour) samples should be collected with a personal sampling pump (with pulsation damper) at a flow rate of 2 liters per minute. Samples should be collected on 0.8 micrometer pore size silver membrane filters (37 mm diameter) preceded by Gelman glass fiber type A-E filters encased in three-piece plastic (polystyrene) field monitor cassettes. The cassette face cap should be on and the plug should be removed. The rotameter should be checked every hour to ensure that proper flow rates are maintained.

A minimum of three full-shift samples should be collected for each job classification, at least one during the night, if applicable. If disparate results are obtained for particular job classifications, sampling should be repeated. It is advisable to sample each shift on more than one day to account for environmental variables (wind, precipitation, etc.), which may affect sampling. Differences in exposures among different work shifts may indicate a need to improve work practices on a particular shift. Sampling results from different shifts for each job classification should not be averaged. Multiple samples from same shift may be used to calculate an average exposure for a particular job classification.

ANALYSIS

The following procedure is for measuring BSFTPM as outlined in the Coke Oven Emissions Standard:

1. All extraction glassware is cleaned with dichromic acid cleaning solution and rinsed with tap water, then deionized water and acetone, and it is allowed to dry completely. It is rinsed with nanograde benzene before use. The Teflon cups are cleaned with benzene and then with acetone.

2. Preweigh 2-ml Perkin-Elmer Teflon cups to 0.01 mg on a suitable balance tare (weight of the cups is about 50 mg).

3. Place the silver membrane filter and glass fiber filter into a 15-ml test tube.

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[a] Federal Register, 1976c.

4. Extract with 5 ml benzene for 5 minutes in an ultrasonic cleaner.

5. Filter the extract in 15-ml medium glass fritted funnels.

6. Rinse test tube and filters with two 1.5-ml aliquots of benzene, and filter through the fritted glass funnel.

7. Collect the extract and two rinses in a 10-ml Kontes graduated evaporative concentrator.

8. Evaporate down to 1 ml while rinsing the sides with benzene.

9. Pipet 0.5 ml into the Teflon cup and evaporate to dryness in a vacuum oven at 40°C for 3 hours.

10. Weigh the Teflon cup. Weight gain is due to the benzene soluble residue in half the sample.

Appendix E. Detailed process information.

The seven coal gasification processes chosen as the basis for this document are briefly described. Accompanying each description are semi-detailed flow sheets of the process and the material balances for strategic points within the process. Each flow sheet is based on a Process and Instrumentation line diagram provided by the management of the pilot plant through the Energy Research and Development Administration, Office of Fossil Energy, Gaseous Fuels Project Branch. The material balances, provided at the same time, have been altered in only two respects:

- To show the possible presence of solids elutriated from the gasifier, where they are not shown in the original balance
- To show the possible presence of coal-derived condensable hydrocarbons and their distribution where they are not shown in the original balance

The material balances supplied with the information from the CO_2 Acceptor, Bi-Gas, and Agglomerating Burner do not indicate the presence of coal-derived condensable hydrocarbons. Information from the CO_2 Acceptor pilot plant operations confirms this lack of condensable hydrocarbons. There is insufficient information from either Bi-Gas or Agglomerating Burner pilot plants to estimate either the quantity or distribution of condensable hydrocarbons in either process.

The HYGAS material balance indicates the presence of light oil throughout the process. There is no indication of its distribution. The MERC Stirred Fixed Bed information also indicates the presence of condensable hydrocarbons, but does not define their distribution. In this latter case all gasifier products are fed to the thermal oxidizer.

Data from the Synthane process indicates that when Pittsburgh seam coal is fed to the unit, 212 pounds per hour of condensable hydrocarbons are produced. Bench scale data indicated that 80% of these hydrocarbons were benzene soluble and that no condensate boiling lower than 100°C was produced. This same data gave a boiling point curve for the liquids recovered (see Process discussion of coal gasification). Based on this data the following information was constructed by guesstimation.

Synthane Condensable Hydrocarbon
Guesstimated Properties

	Boiling Range		Avg. Boiling Point		Molecular Weight
	°F	°C	°F	°C	
Light oil	272-400	133-204	336	169	150
Middle oil	400-600	204-316	500	260	190
Heavy oil	600-950	316-510	775	413	230
Residue	+950	+510	950	510	400

The following assumptions were also made:

- 2.5 wt % solids pass through the gasifier cyclone.
- The scrubber circulating oil is a coal derived middle oil.
- There is no change in oil composition at the Shift Conversion unit.
- There is no holdup of oil in the Benfield gas purification system.

METHOD OF CALCULATION

It was assumed that normal vapor-phase pressure-temperature relationships held throughout the system. The vapor pressure was calculated from the "Vapor Pressure Chart" as shown in the Journal of the Institute of Petroleum Technology 23-311 (1937).* It was further assumed that the gas streams could not contain condensable hydrocarbons in excess of the saturation limits of the gas. The results of these assumptions are indicated in the material balances for the Synthane unit.

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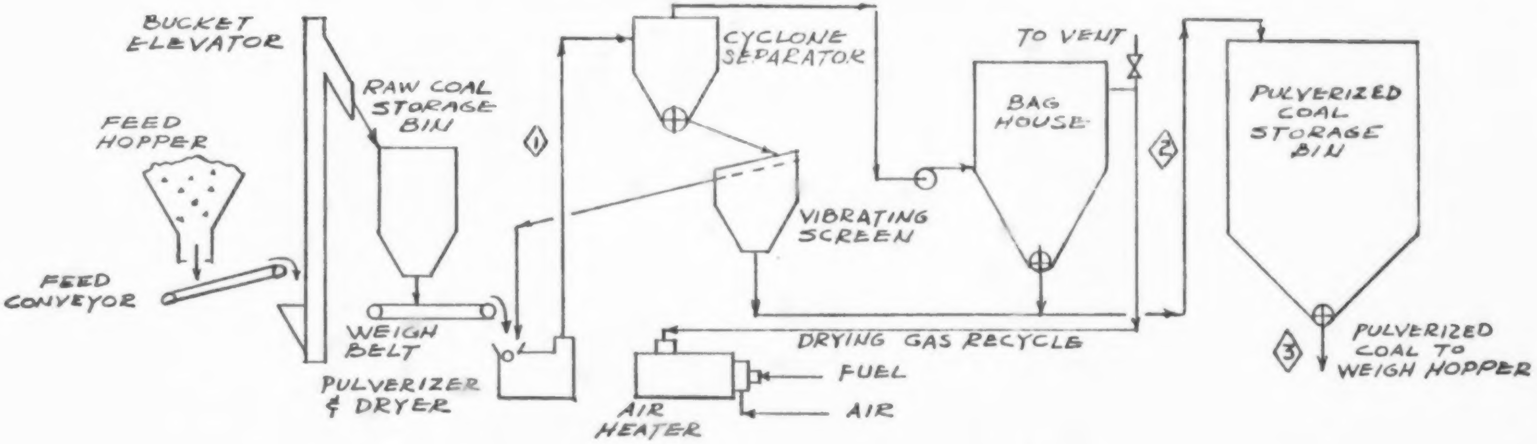
* This data was confirmed by J.M. Evans for hydrocarbon condensates derived by coal liquefaction under an Office of Coal Research contract with Consolidation Coal Co., R&D Division, November 24, 1964.

SYNTHANE

Coal dried and crushed to a 0.03-inch diameter (minus 20 mesh) is fed to a Petrocarb lockhopper system. From this lockhopper system it is fed pneumatically, using steam as the carrier fluid, to a fluidized bed pretreater. Steam and a controlled quantity of oxygen are used as the fluidizing medium and oxidant to control pretreater temperature at 800°F (427°C). (Controlled pretreatment to reduce coal agglomeration is a principal feature of the Synthane process.) The pretreated coal overflows into the gasifier.

The gasifier is a vertical, single-stage, fluid-bed reactor with an internal cyclone separator operating at 1500°F (815°C). The fluidized bed is supported by a funnel shaped grid plate with a central char withdrawal pipe. The fluidizing media are steam and oxygen. Coal feed can be located above the bed or in the bed. Char and ash are continuously removed from the bed by a Petrocarb lockhopper system or by an emergency water slurry system.

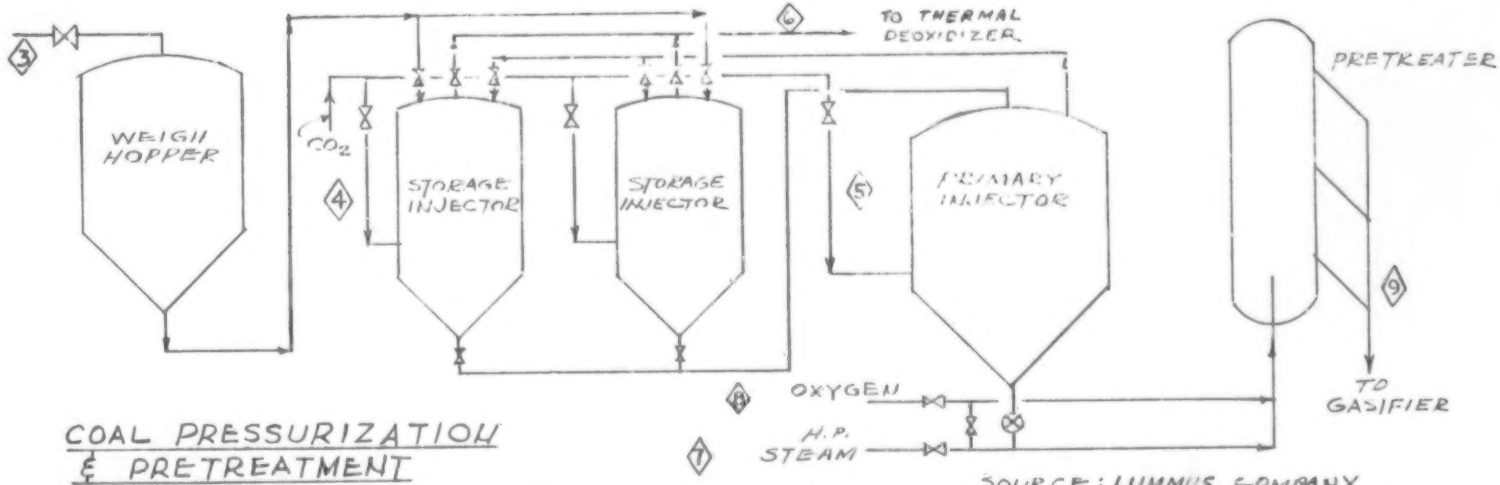
Downstream processes include a conventional water-venturi scrubber plus water wash, carbon monoxide shift unit, Benfield gas purification and both a Tube Wall Reactor and a Hot Gas Recycle methanation system. A Stretford unit is used for sulfur removal.


BUCKET ELEVATOR
FEED HOPPER
FEED CONVEYOR
RAW COAL STORAGE BIN
WEIGH BELT
PULVERIZER & DRYER
1
CYCLONE SEPARATOR
VIBRATING SCREEN
AIR HEATER
FUEL
AIR
DRYING GAS RECYCLE
TO VENT
BAG HOUSE
2
PULVERIZED COAL STORAGE BIN
3
PULVERIZED COAL TO WEIGH HOPPER

COAL PREPARATION
SYNTHANE PILOT PLANT

SOURCE: LUMMUS COMPANY DRAWINGS OF 1974.

MATERIAL BALANCE			
Stream Ident.	Pulverized Coal to Cyclone Separator	Pulverized Coal to Storage	Pulverized Coal to Weigh-Hopper
Stream No.	1	2	3
Rate, lbs/hr	10000 cap.	10000 cap.	6150
Analysis			
H_2	-	-	-
CO_2	-	-	-
CH_4	-	-	-
O_2	-	-	-
C_2H_6	-	-	-
N_2	-	-	-
H_2O	-	-	-
CO	-	-	-
Light Oil	-	-	-
Middle Oil	-	-	-
Heavy Oil	-	-	-
MAF Coal	-	-	5541
Moisture	-	-	154
Ash	-	-	455
Total	-	-	6150
Press., psig	Atmos.	Atmos.	Atmos.
Temp., °F	250-300	100-125	100

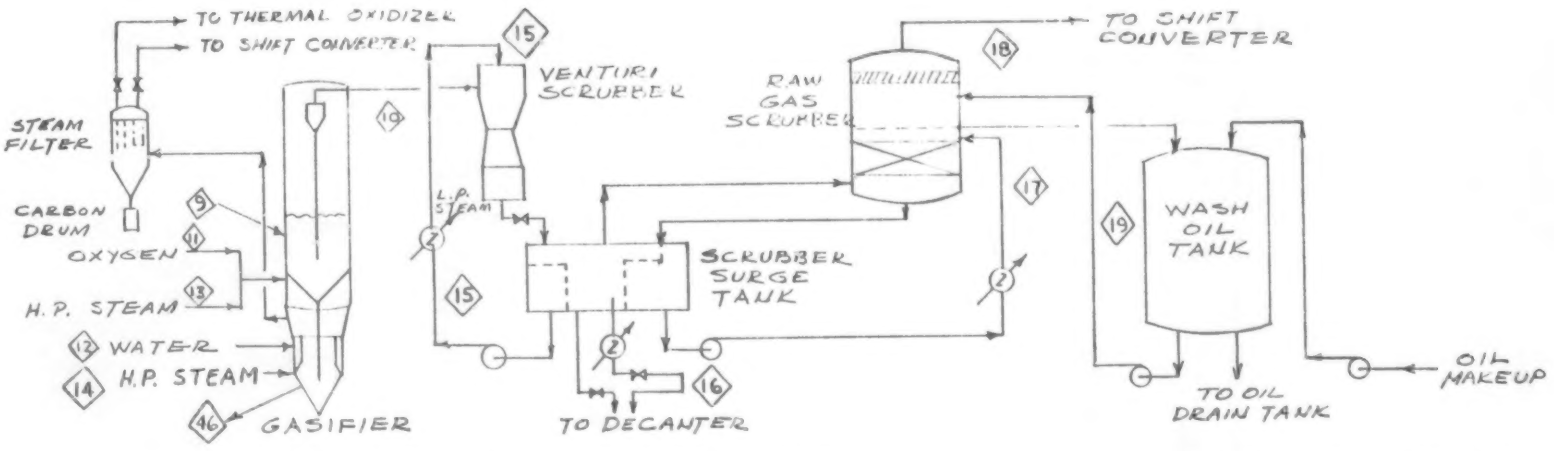

③
WEIGH HOPPER
CO₂
④
STORAGE INJECTOR
STORAGE INJECTOR
⑥
TO THERMAL DEOXIDIZER
⑤
PRIMARY INJECTOR
PRETREATER
⑨
TO GASIFIER
⑧
OXYGEN
⑦
H.P. STEAM

COAL PRESSURIZATION
& PRETREATMENT
SYNTHANE PILOT PLANT

SOURCE: LUMMUS COMPANY DRAWINGS OF 1974

MATERIAL BALANCE							
Stream Ident.	Coal Feed to Weigh-Hopper	CO_2 to Storage Injectors	Feed, CO_2 to Primary Injector	Vent Gas	High Pressure Steam Feed	Oxygen Feed	Gasifier Feed
Stream No.	③	④	⑤	⑥	⑦	⑧	⑨
Rate, lbs/hr	6150	3801*	1946	1855	1633	461	8139
Analysis							
H_2	-	1.2	0.6	0.6	-	-	0.3
CO_2	-	3797	1944	1853	-	-	244.5
CH_4	-	3.3	1.6	1.6	-	-	20.4
O_2	-	-	-	-	-	452.7	-
C_2H_6	-	-	-	-	-	-	2.3
N_2	-	-	-	-	-	8.6	8.6
H_2O	-	-	-	-	1633	-	1786.8
CO	-	-	-	-	-	-	18.2
Light Oil	-	-	-	-	-	-	6.2
Middle Oil	-	-	-	-	-	-	32.0
Heavy Oil	-	-	-	-	-	-	23.3
MAF Coal	5541	-	-	-	-	-	5541
Moisture	154	-	-	-	-	-	-
Ash	455	-	-	-	-	-	455.0
Total	6150	3801	1946	1855	1633	461	8139
Press., psig	Atmos.	1100	1100	-	1100	1100	1000
Temp., °F	100	290	290	-	800	100	800

Note: The sum of the components may not equal the total because of rounding.
*Material balance indicates possibility of traces of light oil when CO_2 discharged from Stretford unit used here.


TO THERMAL OXIDIZER
TO SHIFT CONVERTER
STEAM FILTER
CARBON DRUM
OXYGEN
H.P. STEAM
WATER
H.P. STEAM
GASIFIER
9
11
13
12
14
46
10
15
VENTURI SCRUBBER
L.P. STEAM
15
SCRUBBER SURGE TANK
TO DECANTER
16
RAW GAS SCRUBBER
18
17
TO SHIFT CONVERTER
19
WASH OIL TANK
TO OIL DRAIN TANK
OIL MAKEUP

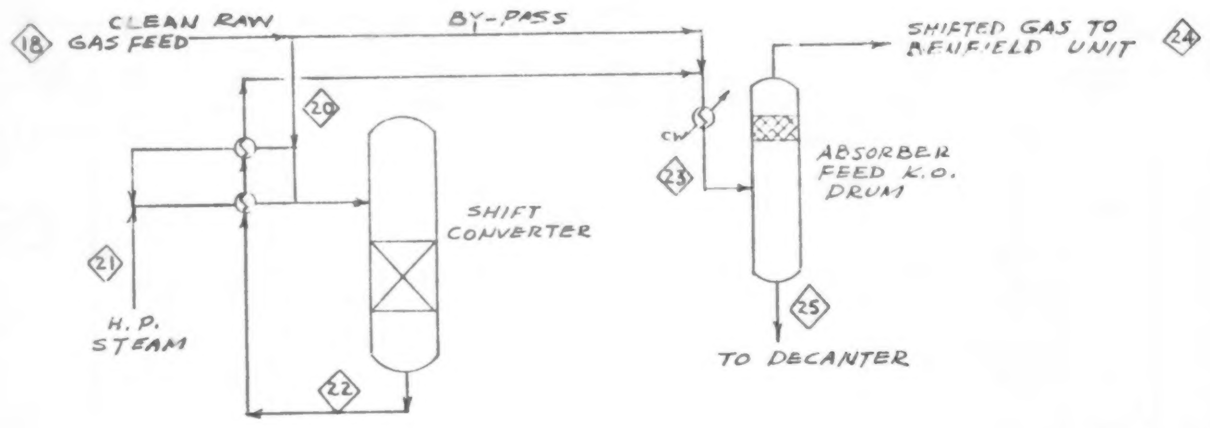
GASIFIER AND OIL SCRUBBER
SYNTHANE PILOT PLANT

SOURCE: LUMMUS COMPANY DRAWINGS OF 1974

MATERIAL BALANCE											
Stream Ident.	Gasifier Feed	Gasifier Outlet Gas	Gasifier O_2 Feed	Gasifier Water Feed	Gasifier Steam Feed	Gasifier Bottom Steam Feed	Venturi Recycle Water Feed	Fluid Stream to Decanter	Scrubber Water Circulation	Scrubber Off-Gas	Scrubber Oil Circulation
Stream No.	9	10	11	12	13	14	15	16	17	18	19
Rate, lbs/hr	8139	15433	1066	800	5909	3109	78230	5549	63970	9899	8600
Analysis											
H_2	0.3	173.8	-	-	-	-	-	-	-	173.8	-
CO_2	244.5	5655.3	-	-	-	-	-	48	766	5606.9	-
CH_4	20.4	1349.0	-	-	-	-	-	-	-	1349.0	-
O_2	-	-	1046.4	-	-	-	-	-	-	-	-
C_2H_6	2.3	81.9	-	-	-	-	-	-	-	81.2	-
N_2	8.6	170.9	19.6	-	-	-	-	-	-	170.9	-
H_2O	1786.8	5907.5	-	800	5909	3109	78230	5170	62500	733.2	-
CO	18.2	1554.5	-	-	-	-	-	-	-	1554.5	-
Light Oil	6.2	10.6	-	-	-	-	-	-	-	10.6	-
Middle Oil	32.0	61.5	-	-	-	-	-	-	-	82.0	8600
Heavy Oil	23.3	55.1	-	-	-	-	-	55.0	-	0.1	-
NH_3	-	86.8	-	-	-	-	-	42	704	44.3	-
H_2S	-	92.0	-	-	-	-	-	-	-	92.0	-
Residue	-	84.8	-	-	-	-	-	84.1	-	Trace	-
Coal & Fines	5996.5	150.0	-	-	-	-	-	150.0	-	-	-
Total	8139	15433	1066	800	5909	3109	78230	5549	63970	9899	8600
Press., psig	1000	1000	1100	975	1100	1100	1080	1000	1010	990	1010
Temp., °F	800	1400	100	167	800	800	350	396	320	330	330

Note: The sum of the components may not equal the total because of rounding.

MATERIAL BALANCE	
Stream Ident.	Gasifier Char Outlet
Stream No.	46
Rate, lbs/hr	1831
Analysis	
H	18
CO_2	-
CH_4	-
O	33
C_2H_6	-
N	9
H_2O	-
C	1325
Light Oil	-
Middle Oil	-
Heavy Oil	-
NH_3	-
S	8
Ash	438
Coal & Fines	-
Total	1831
Press., psig	1000
Temp., °F	600

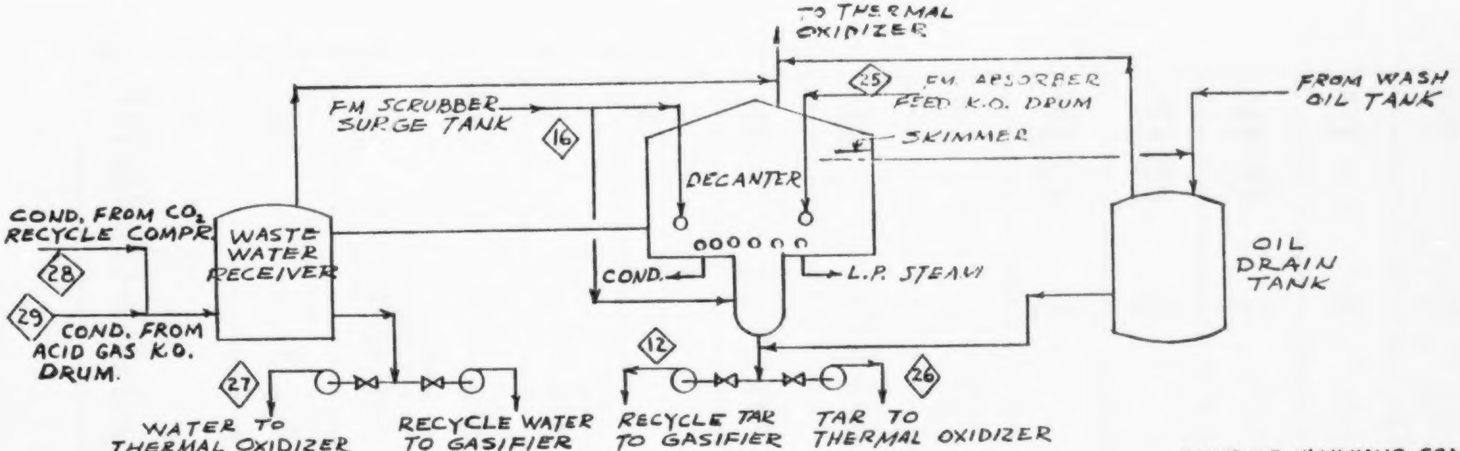

18
CLEAN RAW GAS FEED
BY-PASS
SHIFTED GAS TO BENFIELD UNIT
24
20
CW
23
ABSORBER FEED K.O. DRUM
SHIFT CONVERTER
21
H.P. STEAM
25
TO DECANTER
22

SHIFT CONVERTER
SYNTHANE PILOT PLANT

SOURCE: LUMMUS COMPANY DRAWINGS OF 1974

MATERIAL BALANCE							
Stream Ident.	Scrubber Off-Gas	Off-Gas Fraction for Conversion	High Pressure Steam for Conversion	Converted Off-Gas Stream	Off-Gas and Converted Gas	Converted Gas for Purification	Condensate from Converter
Stream No.	18	20	21	22	23	24	25
Rate, lbs/hr	9899	4951	2198	7149	12097	9315	2779
Analysis							
H_2	173.8	86.9	-	128.8	215.7	215.7	-
CO_2	5606.9	2803.4	-	3718.9	6522.3	6412.3	110
CH_4	1349.0	674.5	-	674.5	1349.0	1349.0	-
O_2	-	-	-	-	-	-	-
C_2H_6	81.2	40.6	-	40.6	81.2	81.2	-
N_2	170.9	85.5	-	85.5	171.0	171.0	-
H_2O	733.2	366.6	2198	2189.8	2556.5	14.4	2540
CO	1554.5	778.7	-	196.1	972.0	972.0	-
Light Oil	10.6	5.3	-	5.3	10.6	10.6	-
Middle Oil	82.0	41.0	-	41.0	82.0	0.16	81.8
Heavy Oil	0.1	0.05	-	0.05	0.1	-	0.1
NH_3	44.3	22.1	-	22.1	44.2	-	44
H_2S	92.0	46.0	-	46.0	92.0	88.6	3
Residue	-	Trace	-	Trace	Trace	-	Trace
Total	9899	4951	2198	7149	12097	9315	2779
Press., psig	990	990	990	980	970	965	970
Temp., °F	330	330	600	825	447	125	125

Note: The sum of the components may not equal the total because of rounding.

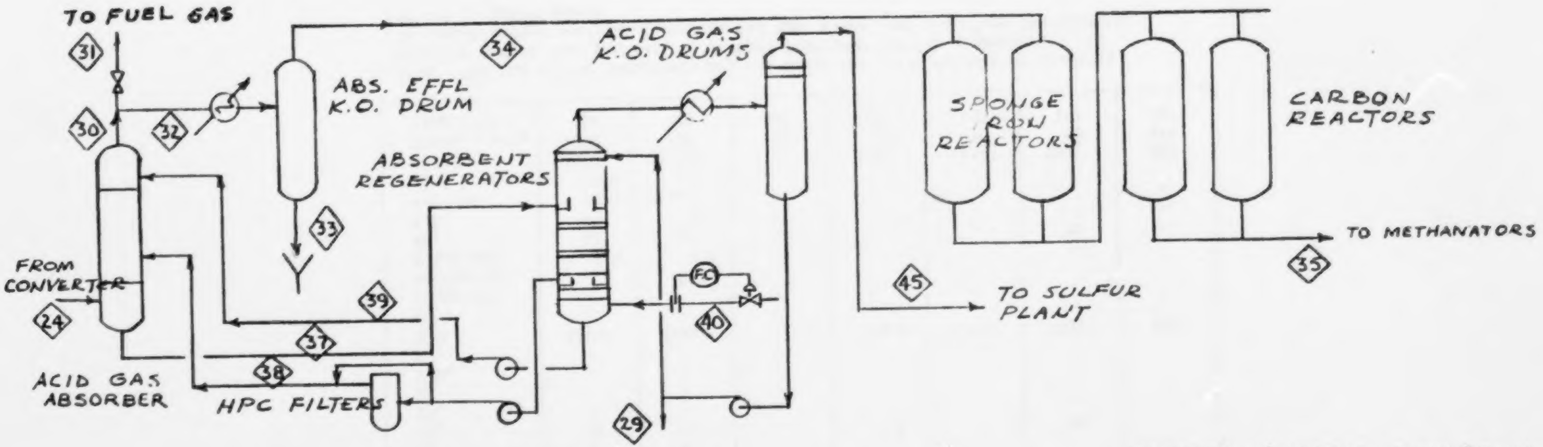

TO THERMAL OXIDIZER
FROM WASH OIL TANK
FM SCRUBBER SURGE TANK
16
25
FM. ABSORBER FEED K.O. DRUM
SKIMMER
DECANTER
COND. FROM CO2 RECYCLE COMPR.
28
WASTE WATER RECEIVER
29
COND. FROM ACID GAS K.O. DRUM.
COND.
L.P. STEAM
OIL DRAIN TANK
12
27
26
WATER TO THERMAL OXIDIZER
RECYCLE WATER TO GASIFIER
RECYCLE TAR TO GASIFIER
TAR TO THERMAL OXIDIZER

DECANTER AND WASTE STREAM RECOVERY
SYNTHANE PILOT PLANT

SOURCE: LUMMUS COMPANY
DRAWINGS OF 1974

MATERIAL BALANCE							
Stream Ident.	Fluid from Surge Tank to Decanter	Condensate from Converted Gas	Tar to Thermal Oxidizer	CO_2 Compressor Condensate	Acid Gas Condensate	Wastewater to Thermal Oxidizer	Recycle Tar to Gasifier
Stream No.	16	25	26	28	29	27	12
Rate, lbs/hr	5492	2779	*	100	1714	8971	800
Analysis							
H_2	-	-	-	-	-	-	-
CO_2	48	110	-	0.5	-	158	-
CH_4	-	-	-	-	-	-	-
O_2	-	-	-	-	-	-	-
C_2H_6	-	-	-	-	-	-	-
N_2	-	-	-	-	-	-	-
H_2O	5170*	2540	*	99.5	1714	8724*	800*
CO	-	-	-	-	-	-	-
Light Oil	-	-	-	-	-	-	-
Middle Oil	-	81.8	-	-	-	-	-
Heavy Oil	5.5	0.1	-	-	-	-	-
NH_3	42	44	-	-	-	86	-
H_2S	-	3	-	-	-	3	-
Residue	76.3	Trace	-	-	-	-	-
Coal & Fines	150.0	-	-	-	-	-	-
Total	5492	2779	-	100	1714	8971	800
Press., psig	1000	970	50	0.5	50	50	975
Temp., °F	396	125	180	100	150	147	167

Note: The sum of the components may not equal the total because of rounding.
*Decanter liquid feed pressure is dropped from 1000 psig to atmospheric. It is probable that emulsion formation may take place, and therefore the quantity of oil is questionable.


TO FUEL GAS
31
30
32
ABS. EFFL K.O. DRUM
34
ACID GAS K.O. DRUMS
SPONGE IRON REACTORS
CARBON REACTORS
ABSORBENT REGENERATORS
33
FROM CONVERTER
24
39
37
38
ACID GAS ABSORBER
HPC FILTERS
FC
40
29
45
TO SULFUR PLANT
35
TO METHANATORS

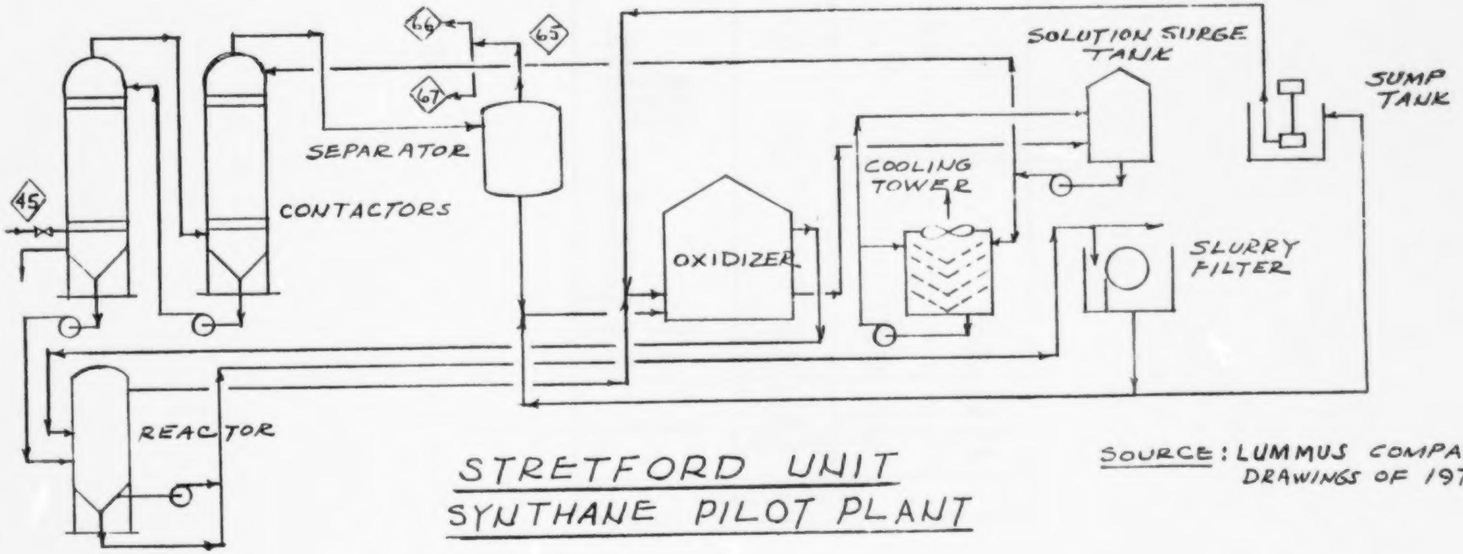
GAS PURIFICATION
SYNTHANE PILOT PLANT

SOURCE: LUMMUS COMPANY DRAWINGS OF 1974

MATERIAL BALANCE

Stream Ident.	Converted Gas	Sweet Gas	Sweet Gas to Fuel Gas	Sweet Gas to Cooler	Sweet Gas Condensate	Sweet Gas to Reactors	Purified Gas to Methanators	Acid Gas to Sulfur Plant	Rich Carbonate Solution	Partially Stripped Carbonate Solution	Regenerated Carbonate Solution	Carbonate Stripper Steam Feed	Acid Gas to Condensate Waste Water
Stream No.	24	30	31	32	33	34	35	45	37	38	39	40	29
Rate, lbs/hr	9315	2899	2029	869	4	864	864	6705	158897	114500	38000	2000	1714
Analysis													
H_2	215.7	214.1	150.0	64.1	-	64.1	64.1	1.6	-	-	-	-	-
CO_2	6412.3	101.2	70.4	30.8	-	30.8	30.8	6311.0	-	-	-	-	-
CH_4	1349.0	1340.9	939.9	401.0	-	401.0	401.0	8.0	-	-	-	-	-
O_2	-	-	-	-	-	-	-	-	-	-	-	-	-
C_2H_6	81.2	81.2	57.1	24.1	-	24.1	24.1	-	-	-	-	-	-
N_2	171.0	171.0	120.5	50.4	-	50.4	50.4	-	-	-	-	-	-
H_2O	14.4	10.8	5.4	3.6	1.5	1.8	1.8	291.9	102001	78110	26473	2000	1714
CO	972.0	969.2	677.8	291.3	-	291.3	291.3	2.8	-	-	-	-	-
Light Oil	10.6	10.6	7.3	3.2	2.46	0.8	-	0.8	-	-	-	-	-
Middle Oil	0.16	0.16	0.09	0.07	0.07	-	-	-	-	-	-	-	-
Heavy Oil	-	-	-	-	-	-	-	-	-	-	-	-	-
H_2S	88.6	-	-	-	-	-	-	88.6	-	-	-	-	-
K_2CO_3	-	-	-	-	-	-	-	-	4882	17630	7400	-	-
$KHCO_3$	-	-	-	-	-	-	-	-	50510	17520	4050	-	-
KHS	-	-	-	-	-	-	-	-	1504	1240	77	-	-
Total	9315	2899	2029	869	4	864	864	6705	158897	114500	38000	2000	1714
Press., psig	965	964	964	964	960	960	940	3	964	1000	1000	6	50
Temp., °F	125	130	130	130	95	95	95	120	217	226	237	300	120

Note: The sum of the components may not equal the total because of rounding.

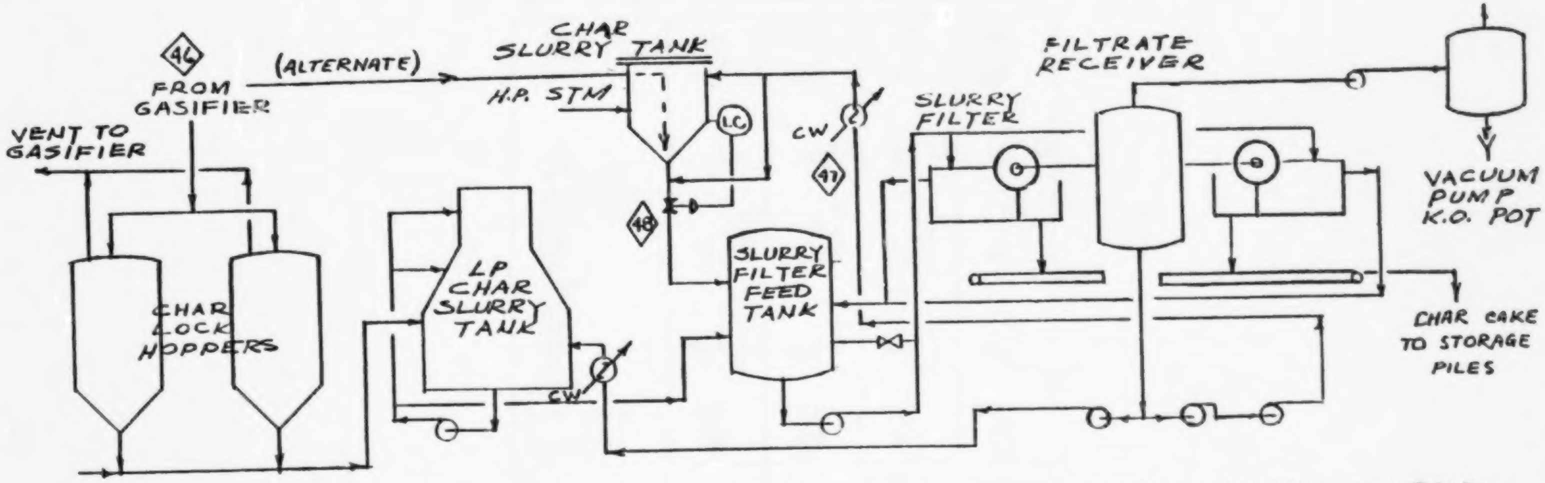

45
66
65
67
SEPARATOR
CONTACTORS
REACTOR
OXIDIZER
COOLING TOWER
SOLUTION SURGE TANK
SUMP TANK
SLURRY FILTER

STRETFORD UNIT
SYNTHANE PILOT PLANT

SOURCE: LUMMUS COMPANY DRAWINGS OF 1974

MATERIAL BALANCE				
Stream Ident.	Acid Gas	Treated Gas	Off-Gas to CO_2 Recycle	Off-Gas to Thermal Oxidizer
Stream No.	45	65	66	67
Rate, lbs/hr	6705	6531	3176	3355
Analysis				
H_2	1.6	1.6	0.8	0.8
CO_2	6311.0	6311.0	3068.7	3242.3
CH_4	8.0	8.0	3.9	4.1
O_2	-	-	-	-
C_2H_6	-	-	-	-
N_2	-	-	-	-
H_2O	291.9	207.2	100.3	106.4
CO	2.8	2.8	1.4	1.4
Light Oil	0.8	0.8	0.4	0.4
Middle Oil	-	-	-	-
Heavy Oil	-	-	-	-
H_2S	88.6	150 ppm	150 ppm	150 ppm
Total	6705	6531	3176	3355
Press., psig	3	1	1	1
Temp., °F	120	105	105	105

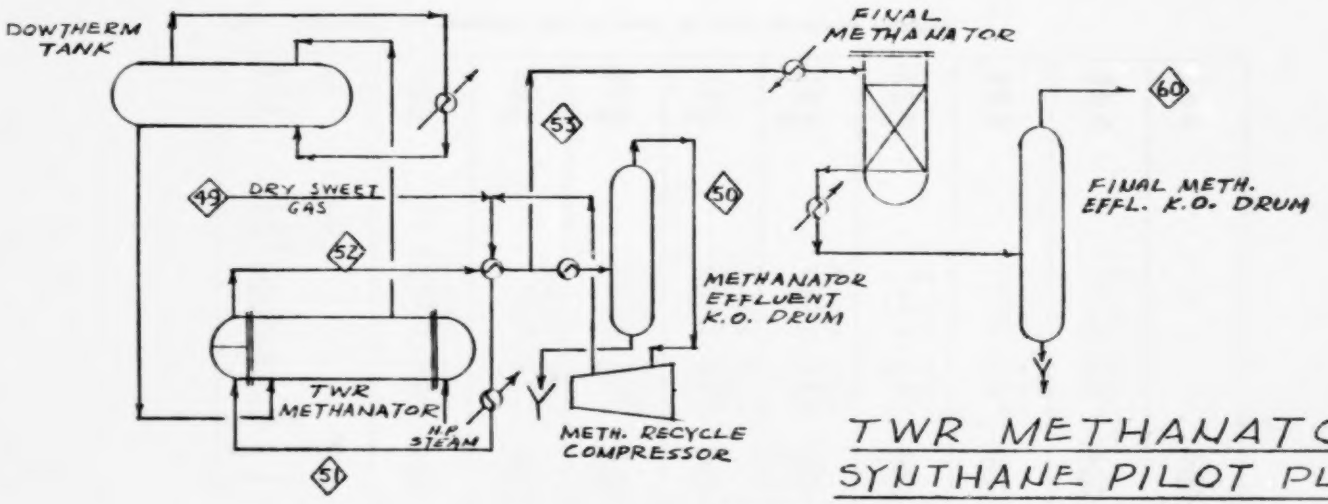
Note: The sum of the components may not equal the total because of rounding.


46
FROM GASIFIER
VENT TO GASIFIER
(ALTERNATE)
CHAR SLURRY TANK
H.P. STM
LC
CW
47
48
CHAR LOCK HOPPERS
LP CHAR SLURRY TANK
CW
SLURRY FILTER FEED TANK
SLURRY FILTER
FILTRATE RECEIVER
VACUUM PUMP K.O. POT
CHAR CAKE TO STORAGE PILES

CHAR REMOVAL UNIT
SYNTHANE PILOT PLANT

SOURCE: LUMMUS COMPANY DRAWINGS OF 1974

MATERIAL BALANCE			
Stream Ident.	Gasifier Char Outlet	Slurry Filtrate	Char Slurry Tank Outlet
Stream No.	46	47	48
Rate, lbs/hr	1831	23450	25981
Analysis			
H	18	-	-
CO_2	-	-	-
CH_4	-	-	-
O	33	-	-
C_2H_6	-	-	-
N	9	-	-
H_2O	-	23400	24100
C	1325	-	-
Light Oil	-	-	-
Middle Oil	-	-	-
Heavy Oil	-	-	-
Char	-	50	1881
Ash	438	-	-
S	8	-	-
Total	1831	23450	25981
Press., psig	1000	15	1090
Temp., °F	600	160	165

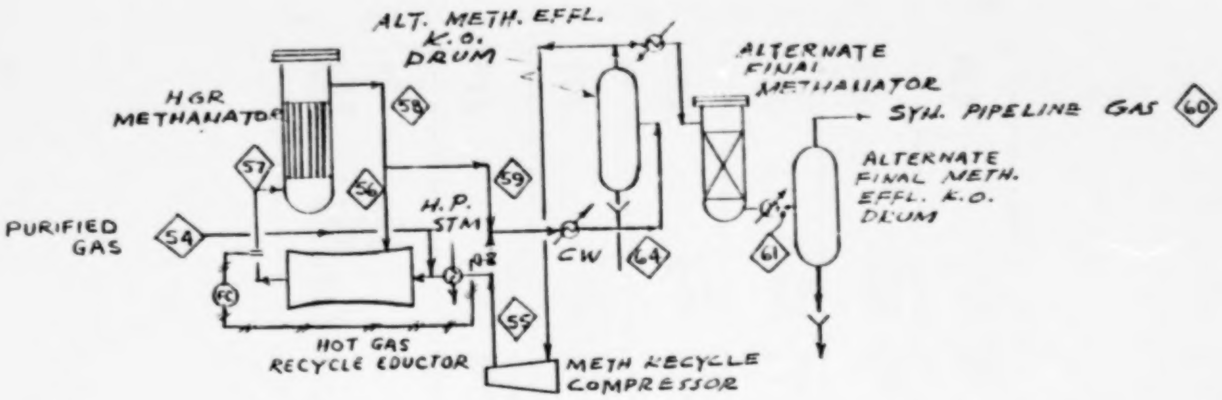

DOWTHERM TANK
DRY SWEET GAS
49
52
53
51
50
60
TWR METHANATOR
H.P. STEAM
METH. RECYCLE COMPRESSOR
METHANATOR EFFLUENT K.O. DRUM
FINAL METHANATOR
FINAL METH. EFFL. K.O. DRUM

TWR METHANATOR
SYNTHANE PILOT PLANT

SOURCE: LUMMUS COMPANY DRAWINGS OF 1974.

MATERIAL BALANCE						
Stream Ident.	Purified Gas to TWR Methanator	Methanated Gas to Recycle	Gas Feed to TWR Methanator	TWR Methanator Outlet Gas	Cold Product Gas	Product Gas
Stream No.	49	50	51	52	53	60
Rate, lbs/hr	432	612	1044	1044	371	338
Analysis						
H_2	32.0	1.3	33.4	2.0	0.7	0.7
CO_2	15.4	27.7	43.1	43.1	15.4	15.4
CH_4	200.5	513.6	714.1	797.2	283.6	283.6
O_2	-	-	-	-	-	-
C_2H_6	12.0	22.0	34.0	34.0	12.0	12.0
N_2	25.2	45.7	70.9	70.9	25.2	25.2
H_2O	0.9	0.9	1.8	95.1	33.9	0.5
CO	145.7	1.1	146.8	1.7	0.6	0.6
Light Oil	-	-	-	-	-	-
Middle Oil	-	-	-	-	-	-
Heavy Oil	-	-	-	-	-	-
Total	432	612	1044	1044	371	338
Press., psig	940	920	940	939	920	900
Temp., °F	95	100	710	715	220	100

Note: The sum of the components may not equal the total because of rounding.


ALT. METH. EFFL. K.O. DRUM
HGR METHANATOR
PURIFIED GAS
54
57
56
58
59
H.P. STM
FC
HOT GAS RECYCLE EDUCTOR
55
METH RECYCLE COMPRESSOR
CW
64
ALTERNATE FINAL METHANATOR
61
SYN. PIPELINE GAS
60
ALTERNATE FINAL METH. EFFL. K.O. DRUM

HGR METHANATOR
SYNTHANE PILOT PLANT

SOURCE: LUMMUS COMPANY DRAWINGS OF 1974

MATERIAL BALANCE									
Stream Ident.	Purified Gas to HGR Methanator	Recycle Methanated Gas	HGR Methanated Gas to Recycle	Gas Feed to HGR Methanator	HGR Methanator Outlet Gas	Hot Product Gas	Product Gas	Final Methanator Gas Feed (HGR)	Alternate Effluent Drum Condensate
Stream No.	54	55	56	57	58	59	60	61	64
Rate, lbs/hr	432	1837	8012	10281	10281	2269	338	339	93
Analysis									
H_2	32.0	4.0	16.5	52.5	21.2	4.7	0.7	1.1	-
CO_2	15.4	83.6	350.3	449.3	449.3	99.0	15.4	15.4	-
CH_4	200.5	1540.8	6439.7	8181.0	8264.1	1824.4	283.6	282.6	-
O_2	-	-	-	-	-	-	-	-	-
C_2H_6	12.0	65.6	274.2	351.8	351.8	77.6	12.0	12.0	-
N_2	25.2	137.0	573.6	735.8	735.8	162.2	25.2	25.2	-
H_2O	0.9	2.9	343.4	347.1	440.5	97.1	0.5	0.5	93
CO	145.7	3.4	14.0	163.1	17.9	3.9	0.6	2.2	-
Light Oil	-	-	-	-	-	-	-	-	-
Middle Oil	-	-	-	-	-	-	-	-	-
Heavy Oil	-	-	-	-	-	-	-	-	-
Total	432	1837	8012	10281	10281	2269	338	339	93
Press., psig	940	950	915	916	915	915	900	900	900
Temp., °F	95	107	765	700	765	765	100	600	100

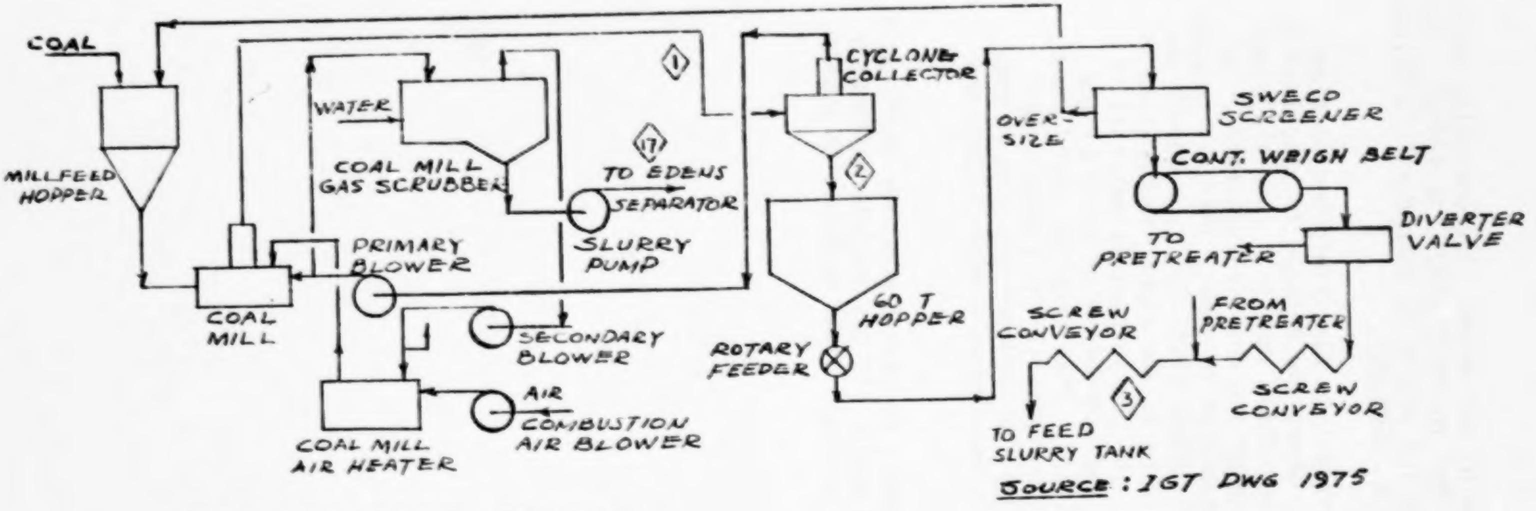
Note: The sum of the components may not equal the total because of rounding.

HYGAS (STEAM-OXYGEN CONFIGURATION)

Coal is crushed to 0.125-inch diameter (6 mesh) and dried. Agglomerating coals are pretreated at atmospheric pressure and 750° to 800°F (400°C to 427°C). The prepared coal is then mixed with toluene and the slurry is pumped with a Wilson Snyder pump to the reactor pressure of 1000 to 1500 psi.

The hydrogasifier is a vertical reactor divided into four fluid-bed sections. The coal slurry is fed into the top section, where the toluene is vaporized by the 1300°F (705°C) gas from stage two and the solids then fall into stage two. In stage two light ends and reactive portions of the coal are gasified. The partially gasified coal then falls down a standpipe to a pot, where is is pneumatically lifted to stage three by the 1700°-1800°F (925°-980°C) producer gas from stage four. The "instantaneous" transition to the higher temperature is claimed to reduce production of heavy oils. The heavy volatile material is gasified in this section as is a portion of the hydrogen-rich solid by the hydrogen-rich producer gas from the fourth stage. Char from the third stage overflows into the fourth stage, where it is burned with the steam-oxygen fluidizing gas to produce the process heat and the producer gas used in the other stages. The unreacted residual char is removed as a water slurry and filtered.

Downstream processes include a venturi scrubber, no carbon monoxide shift unit, a diglycolamine gas purification system and both a hot gas recycle methanator with a packed bed and the Chem Systems, Inc., liquid phase methanation system. A Claus unit is used for sulfur removal.

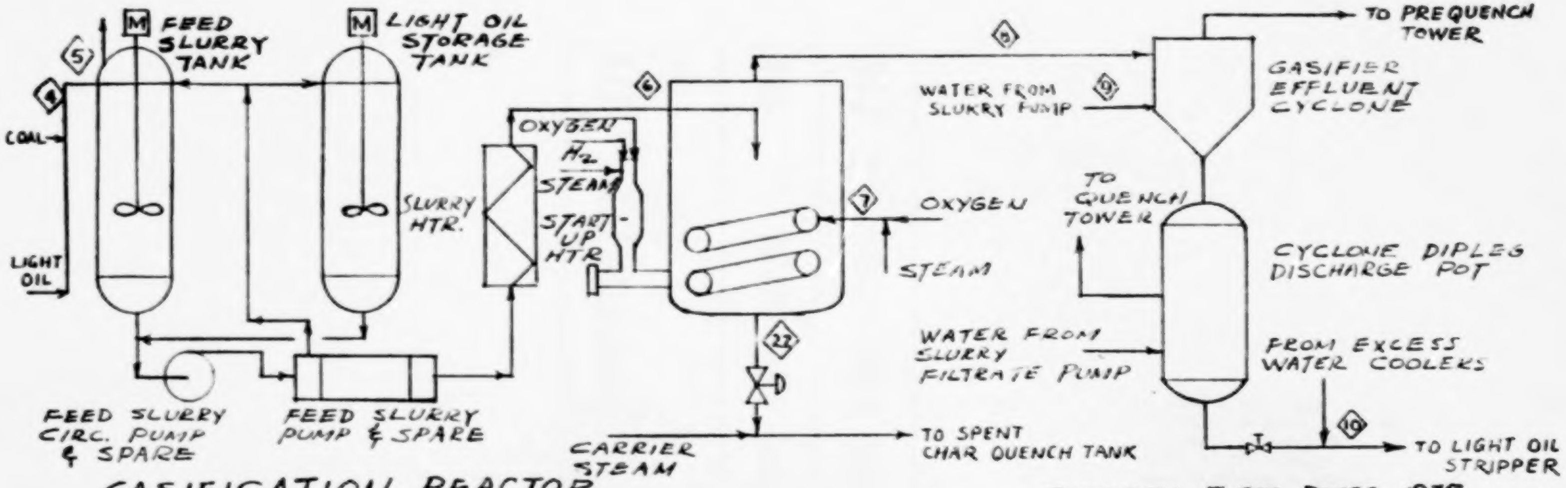

COAL
MILLFEED HOPPER
COAL MILL
WATER
COAL MILL GAS SCRUBBER
PRIMARY BLOWER
1
17
TO EDENS SEPARATOR
SLURRY PUMP
SECONDARY BLOWER
COAL MILL AIR HEATER
AIR
COMBUSTION AIR BLOWER
CYCLONE COLLECTOR
2
60 T HOPPER
ROTARY FEEDER
OVER-SIZE
SWECO SCREENER
CONT. WEIGH BELT
DIVERTER VALVE
TO PRETREATER
FROM PRETREATER
SCREW CONVEYOR
3
SCREW CONVEYOR
TO FEED SLURRY TANK

SOURCE: IGT DWG 1975

HYGAS PILOT PLANT

MATERIAL BALANCE				
Stream Ident.	Pulverized Coal to Cyclone Collector	Pulverized Coal to Storage	Pulverized Coal to Screw Feeder	Coal Dust to Edens Separator
Stream No.	1	2	3	17
Rate, lbs/hr	12200 cap.	12200 cap.	6000	10125
Analysis				
H_2	-	-	-	-
CO_2	-	-	-	-
CH_4	-	-	-	-
O_2	-	-	-	-
C_2H_6	-	-	-	-
N_2	-	-	-	-
H_2O	-	-	-	10000
CO	-	-	-	-
Light Oil	-	-	-	-
Middle Oil	-	-	-	-
Heavy Oil	-	-	-	-
MAF Coal	-	-	4742	198
Ash	-	-	622	13
Moisture	-	-	636	13
S	-	-	-	1
Total	-	-	6000	10125
Press., psig	< Atmos.	-	Atmos.	Atmos.
Temp., °F	300	-	-	-

NOTE: Material balance based on data presented in paper given at the seventh Synthetic Pipeline Gas symposium by Bernard S. Lee, October 27-29, 1975.



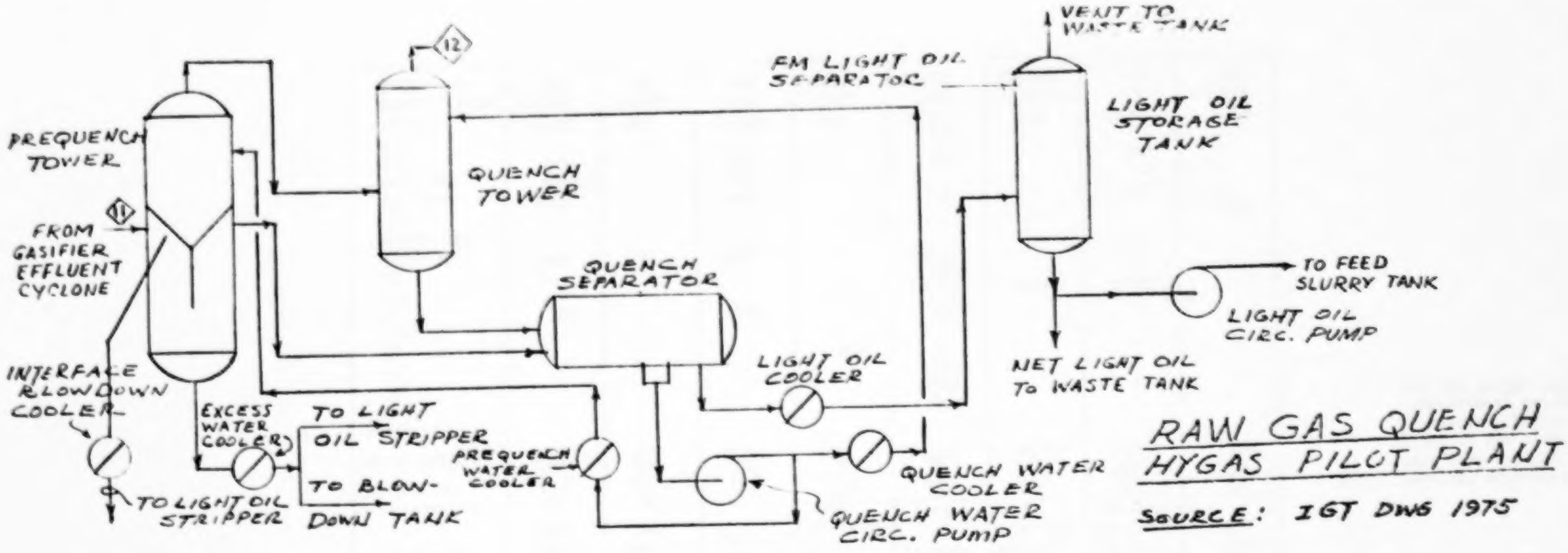
5
4
COAL
LIGHT OIL
M
FEED SLURRY TANK
M
LIGHT OIL STORAGE TANK
SLURRY HTR.
FEED SLURRY CIRC. PUMP & SPARE
FEED SLURRY PUMP & SPARE
OXYGEN
H_2
STEAM
START UP HTR
6
7
OXYGEN
STEAM
22
CARRIER STEAM
TO SPENT CHAR QUENCH TANK
8
TO PREQUENCH TOWER
WATER FROM SLURRY PUMP
9
GASIFIER EFFLUENT CYCLONE
TO QUENCH TOWER
CYCLONE DIPLEG DISCHARGE POT
WATER FROM SLURRY FILTRATE PUMP
FROM EXCESS WATER COOLERS
10
TO LIGHT OIL STRIPPER

GASIFICATION REACTOR
HYGAS PILOT PLANT

SOURCE: IGT DWGS 1975

MATERIAL BALANCE								
Stream Ident.	Feed to Slurry Tank	Vent from Slurry Tank	Feed to Gasifier	Sparger to Gasifier	Gasifier Overhead to Cyclone	Water to Cyclone	Effluent Stream Gasifier to Discharge Pot	Spent Char
Stream No.	4	5	6	7	8	9	10	22
Rate, lbs/hr	17801	605	17196	7971	24211	4626	21932	1320
Analysis								
H_2	-	-	-	-	150	-	-	-
CO_2	-	-	-	-	3265	-	-	-
CH_4	-	-	-	-	627	-	-	-
O_2	-	-	-	795	-	-	-	-
C_2H_6	-	-	-	-	23	-	-	-
N_2	396	-	396	-	396	-	-	-
H_2O	-	-	-	7176	6573	4626	10098	-
CO	-	-	-	-	589	-	-	-
Light Oil	11405	605	10800	-	12271	-	11531	-
Middle Oil	-	-	-	-	-	-	-	-
Char	-	-	-	-	-	-	-	1320
MAF coal	4742	-	4742	-	195	-	195	-
Moisture	636	-	636	-	-	-	5	-
Ash	622	-	622	-	103	-	103	-
H_2S	-	-	-	-	19	-	-	-
Total	17801	605	17196	7971	24211	4626	21932	1320
Press., psig	Atmos.	Atmos.	1100	1520	1050	1000	30	1150
Temp., °F	300	300	300	1133	650	Ambient	150	1509

NOTE: Material balance based on data presented in paper given at the seventh Synthetic Pipeline Gas symposium by Bernard S. Lee, October 27-29, 1975.

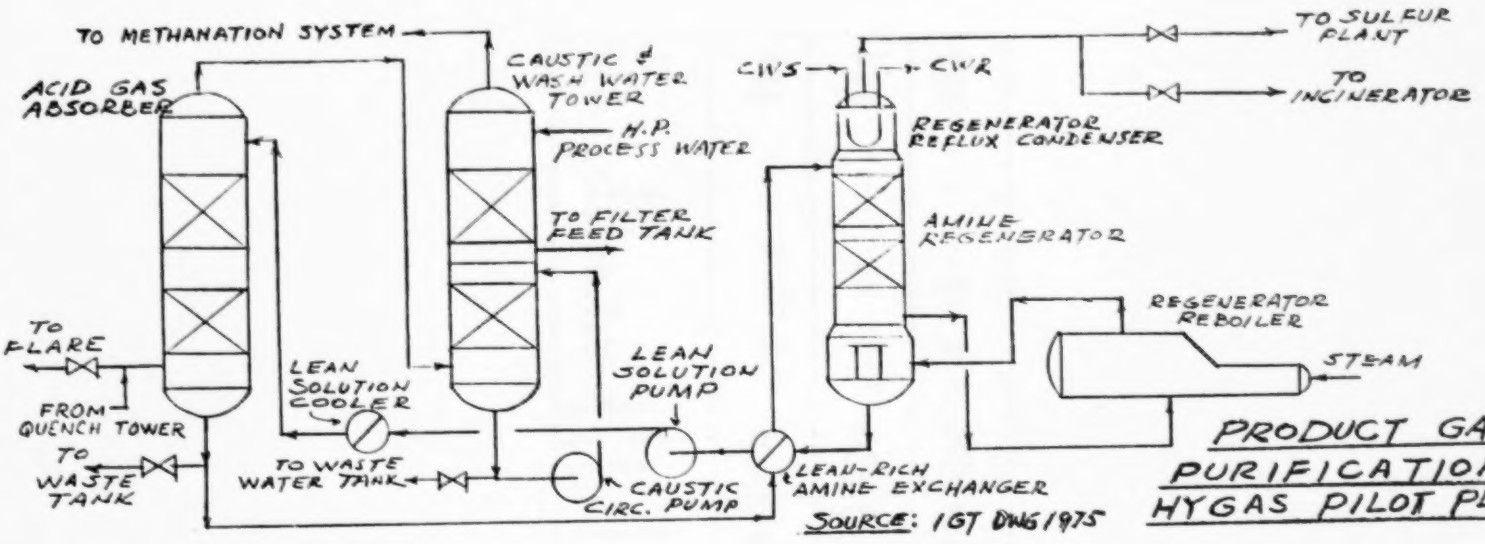

PREQUENCH TOWER
FROM GASIFIER EFFLUENT CYCLONE
11
12
QUENCH TOWER
QUENCH SEPARATOR
FM LIGHT OIL SEPARATOR
VENT TO WASTE TANK
LIGHT OIL STORAGE TANK
TO FEED SLURRY TANK
LIGHT OIL CIRC. PUMP
NET LIGHT OIL To WASTE TANK
INTERFACE BLOWDOWN COOLER
TO LIGHT OIL STRIPPER
EXCESS WATER COOLER
TO LIGHT OIL STRIPPER
TO BLOW-DOWN TANK
PREQUENCH WATER COOLER
LIGHT OIL COOLER
QUENCH WATER COOLER
QUENCH WATER CIRC. PUMP

RAW GAS QUENCH
HYGAS PILOT PLANT

SOURCE: IGT DWG 1975

MATERIAL BALANCE		
Stream Ident.	Effluent Stream to Quench System	Effluent Quench Tower to Purification
Stream No.	11	12
Rate, lbs/hr	6910	5065
Analysis		
H_2	150	150
CO_2	3265	3262
CH_4	627	627
O_2	-	-
C_2H_6	23	23
N_2	396	396
H_2O	1101	-
CO	589	588
Light Oil	740	-
Middle Oil	-	-
Heavy Oil	-	-
H_2S	19	19
S	-	ppm
Total	6910	5065
Press., psig	1000	975
Temp., °F	600	140

NOTE: Material balance based on data presented in paper given at the seventh Synthetic Pipeline Gas symposium by Bernard S. Lee, October 27-29, 1975

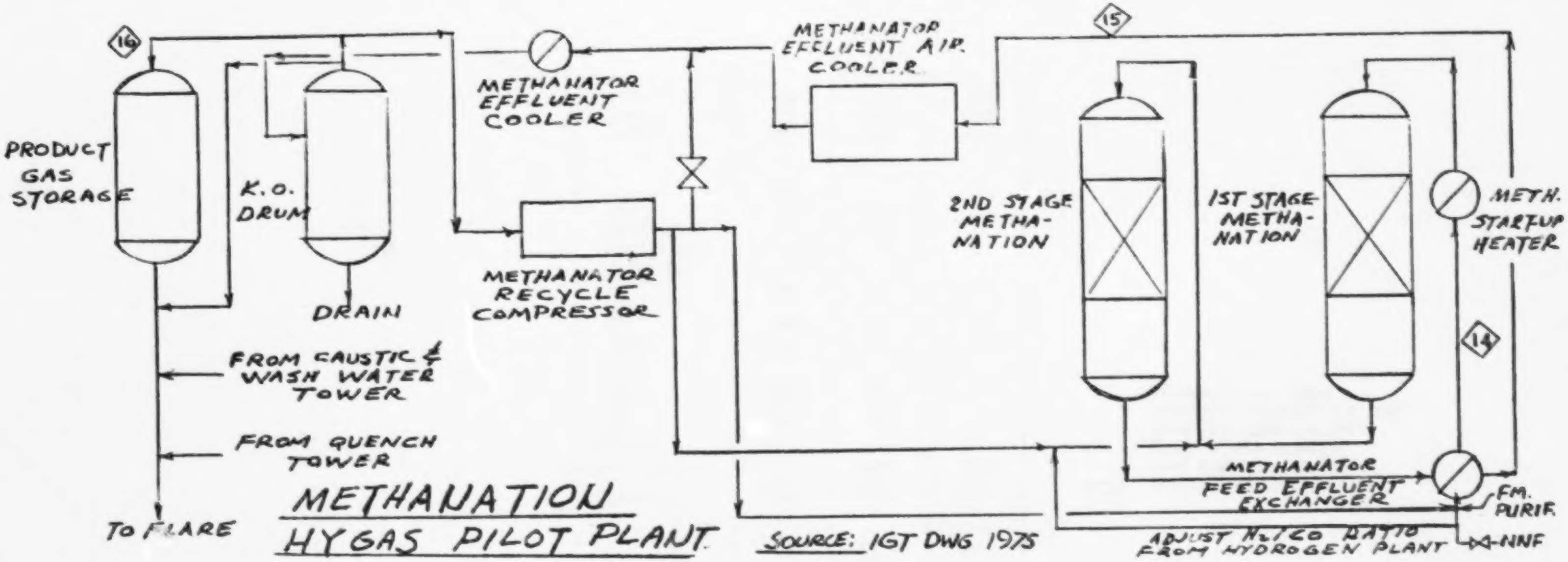

TO METHANATION SYSTEM
ACID GAS ABSORBER
CAUSTIC & WASH WATER TOWER
H.P. PROCESS WATER
TO FILTER FEED TANK
TO FLARE
FROM QUENCH TOWER
TO WASTE TANK
LEAN SOLUTION COOLER
TO WASTE WATER TANK
LEAN SOLUTION PUMP
CAUSTIC CIRC. PUMP
CWS
CWR
REGENERATOR REFLUX CONDENSER
AMINE REGENERATOR
REGENERATOR REBOILER
STEAM
LEAN-RICH AMINE EXCHANGER
TO SULFUR PLANT
TO INCINERATOR

PRODUCT GAS
PURIFICATION
HYGAS PILOT PLANT

SOURCE: IGT DWG 1975

MATERIAL BALANCE			
Stream Ident.	Effluent Quench Tower to Purification	Scrubbed Gas Effluent	Purified Gas to Methanator
Stream No.	12	13	14
Rate, lbs/hr	5065	1465	1054
Analysis			
H_2	150	83	83
CO_2	3262	411	-
CH_4	627	356	356
O_2	-	-	-
C_2H_6	23	37	37
N_2	396	243	243
H_2O	-	-	-
CO	588	335	335
Light Oil	-	-	-
Middle Oil	-	-	-
Heavy Oil	-	-	-
H_2S	19	-	-
S	ppm	-	-
Total	5065	1465	1054
Press., psig	975	975	975
Temp., °F	140	150	100

NOTE: Material balance based on data presented in paper given at the seventh Synthetic Pipeline Gas symposium by Bernard S. Lee, October 27-29, 1975.

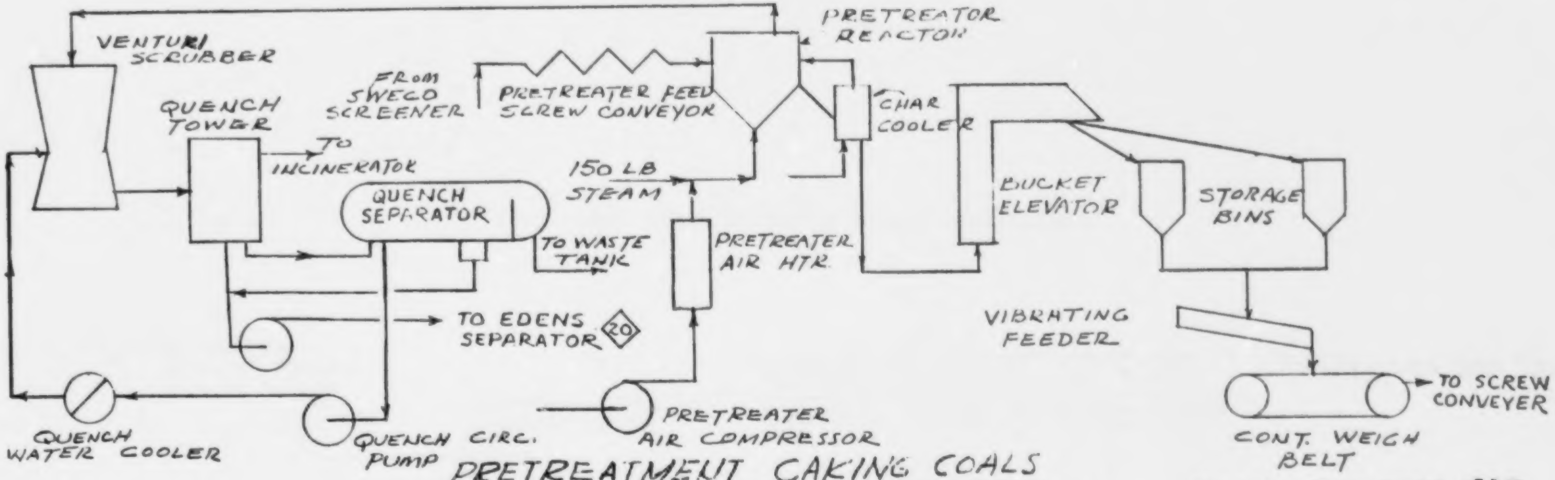

PRODUCT GAS STORAGE
16
K.O. DRUM
DRAIN
METHANATOR EFFLUENT COOLER
METHANATOR RECYCLE COMPRESSOR
METHANATOR EFFLUENT AIR COOLER
15
2ND STAGE METHANATION
1ST STAGE METHANATION
METH. STARTUP HEATER
14
FROM CAUSTIC & WASH WATER TOWER
FROM QUENCH TOWER
TO FLARE
METHANATOR FEED EFFLUENT EXCHANGER
FM. PURIF.
ADJUST H2/CO RATIO FROM HYDROGEN PLANT
NNF

METHANATION

HYGAS PILOT PLANT

SOURCE: IGT DWG 1975

MATERIAL BALANCE			
Stream Ident.	Purified Gas to Methanator	Final Product Gas from Methanator	Final Product Gas to Storage
Stream No.	14	15	16
Rate, lbs/hr	1054	1093	878
Analysis			
H_2	83	14	14
CO_2	-	-	-
CH_4	356	608	608
O_2	-	-	-
C_2H_6	37	-	-
N_2	243	256	256
H_2O	-	215	-
CO	335	-	-
Light Oil	-	-	-
Middle Oil	-	-	-
Heavy Oil	-	-	-
H_2S	-	-	-
S	-	-	-
Total	1054	1093	878
Press., psig	975	1000	1000
Temp., °F	550	300	100

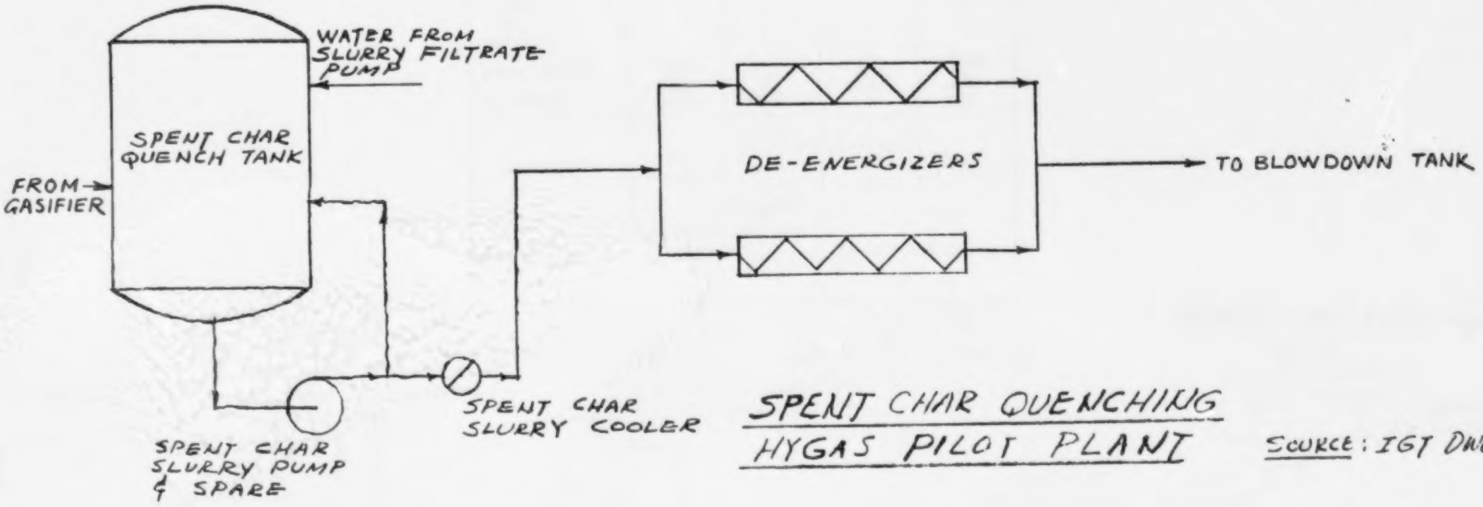

VENTURI SCRUBBER
QUENCH TOWER
FROM SWECO SCREENER
PRETREATER FEED SCREW CONVEYOR
PRETREATOR REACTOR
CHAR COOLER
TO INCINERATOR
150 LB STEAM
QUENCH SEPARATOR
TO WASTE TANK
PRETREATER AIR HTR
BUCKET ELEVATOR
STORAGE BINS
TO EDENS SEPARATOR
20
VIBRATING FEEDER
TO SCREW CONVEYER
QUENCH WATER COOLER
QUENCH CIRC. PUMP
PRETREATER AIR COMPRESSOR
CONT. WEIGH BELT

PRETREATMENT CAKING COALS
HYGAS PILOT PLANT

SOURCE: IGT DWGS 1975

MATERIAL BALANCE				
Stream Ident.	Pretreater Feed	Effluent Gases from Pretreater Reactor	To Edens Separator	To Incinerator
Stream No.	18*	19	20	21
Rate, lbs/hr	6700	9140	186	9960
Analysis				
H_2	-	-	-	-
CO_2	-	457	-	458
CH_4	-	-	-	-
O_2	-	183	-	179
C_2H_6	-	-	-	-
N_2	-	4588	-	4592
H_2O	-	3153	-	4153
CO	-	375	-	379
Light Oil)	-	(73	-	-
Middle Oil	-		-	-
Heavy Oil	-	55	53	-
SO_2	-	119	-	80
Fines	-	137	133	115
	-			-
	-			-
Total	6700	9140	186	9960
Press., psig	Atmos.	5	-	-
Temp., °F	Ambient	800	-	-

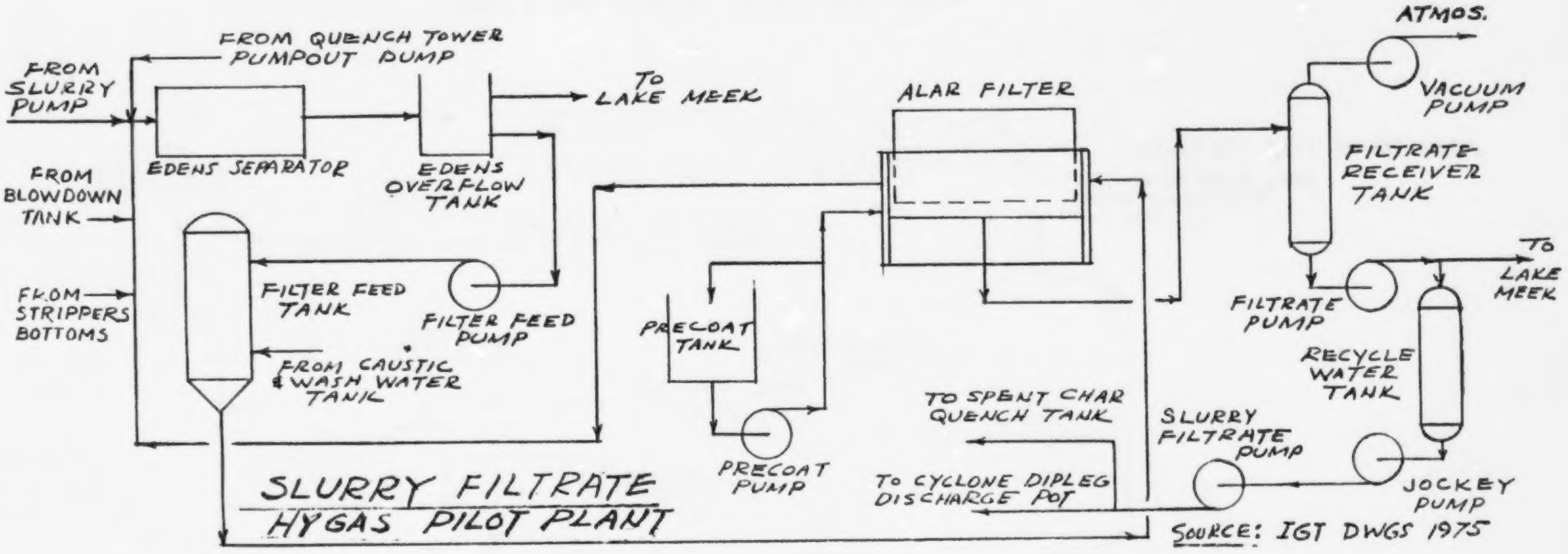
* Dry crushed bituminous coal.


WATER FROM SLURRY FILTRATE PUMP
SPENT CHAR QUENCH TANK
FROM GASIFIER
SPENT CHAR SLURRY PUMP & SPARE
SPENT CHAR SLURRY COOLER
DE-ENERGIZERS
TO BLOWDOWN TANK

SPENT CHAR QUENCHING
HYGAS PILOT PLANT

SOURCE: IGT DWG 1975

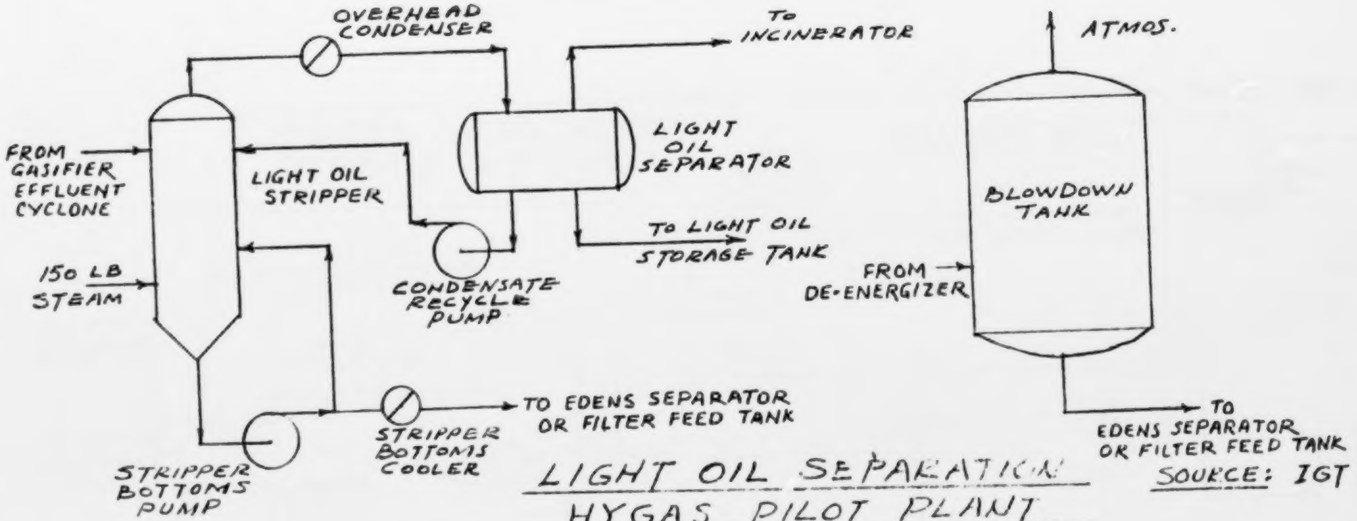
NOTE: No data available to calculate material balance.


FROM QUENCH TOWER PUMPOUT PUMP
FROM SLURRY PUMP
FROM BLOWDOWN TANK
FROM STRIPPERS BOTTOMS
EDENS SEPARATOR
EDENS OVERFLOW TANK
TO LAKE MEEK
FILTER FEED TANK
FILTER FEED PUMP
FROM CAUSTIC & WASH WATER TANK
ALAR FILTER
PRECOAT TANK
PRECOAT PUMP
TO SPENT CHAR QUENCH TANK
TO CYCLONE DIPLEG DISCHARGE POT
ATMOS.
VACUUM PUMP
FILTRATE RECEIVER TANK
FILTRATE PUMP
TO LAKE MEEK
RECYCLE WATER TANK
SLURRY FILTRATE PUMP
JOCKEY PUMP

SLURRY FILTRATE
HYGAS PILOT PLANT

SOURCE: IGT DWGS 1975

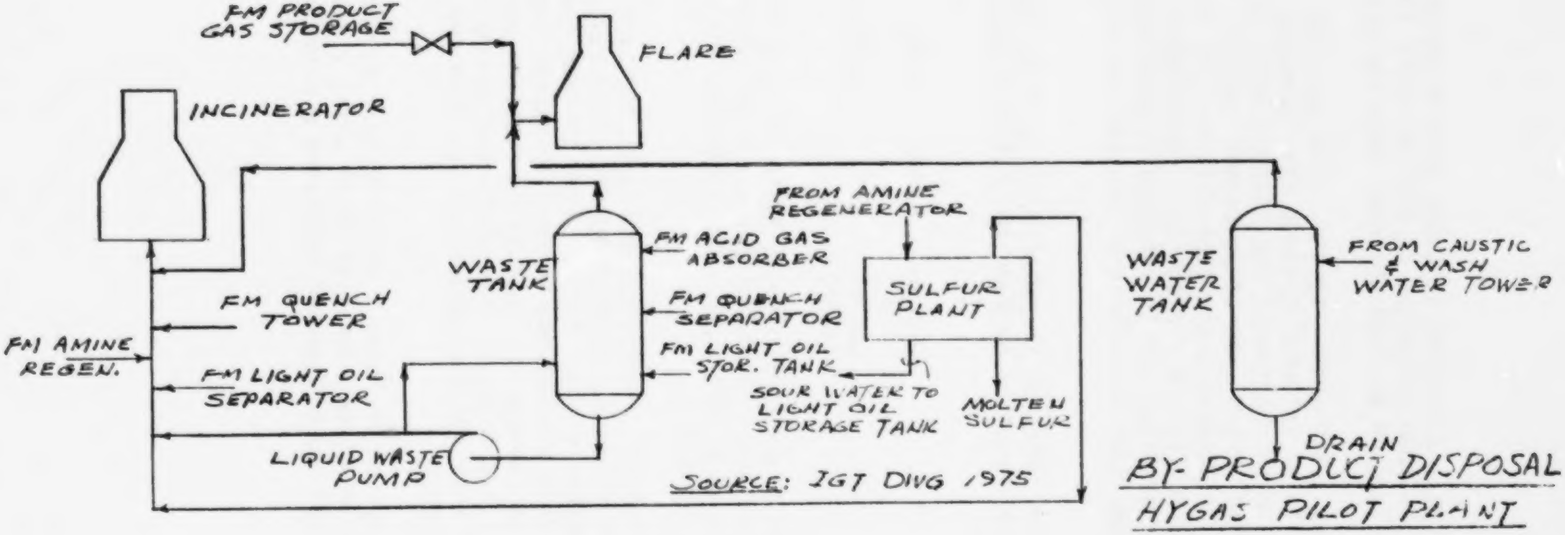
NOTE: No data available to calculate material balance.


OVERHEAD CONDENSER
TO INCINERATOR
ATMOS.
FROM GASIFIER EFFLUENT CYCLONE
LIGHT OIL STRIPPER
LIGHT OIL SEPARATOR
BLOWDOWN TANK
150 LB STEAM
TO LIGHT OIL STORAGE TANK
CONDENSATE RECYCLE PUMP
FROM DE-ENERGIZER
TO EDENS SEPARATOR OR FILTER FEED TANK
TO EDENS SEPARATOR OR FILTER FEED TANK
STRIPPER BOTTOMS PUMP
STRIPPER BOTTOMS COOLER

LIGHT OIL SEPARATION
HYGAS PILOT PLANT

SOURCE: IGT DWGS 1975

NOTE: No data available to calculate material balance.


FM PRODUCT GAS STORAGE
FLARE
INCINERATOR
FROM AMINE REGENERATOR
FM ACID GAS ABSORBER
WASTE TANK
FM QUENCH TOWER
FM QUENCH SEPARATOR
SULFUR PLANT
FM AMINE REGEN.
FM LIGHT OIL SEPARATOR
FM LIGHT OIL STOR. TANK
SOUR WATER TO LIGHT OIL STORAGE TANK
MOLTEN SULFUR
LIQUID WASTE PUMP
WASTE WATER TANK
FROM CAUSTIC & WASH WATER TOWER
DRAIN

BY-PRODUCT DISPOSAL

HYGAS PILOT PLANT

SOURCE: IGT DWG 1975

NOTE: No data available to calculate material balance.

CO_2 ACCEPTOR

Lignite or sub-bituminous coal is crushed to 0.006-inch diameter (minus 100 mesh) and dried. The coal is then preheated to 350° to 500°F (178° to 260°C). A normal lockhopper system is used to feed the coal into the gasifier.

The CO_2 Acceptor system uses a two-vessel system. The gasifier is a single-stage, fluid-bed reactor with an internal cyclone that operates at 1520°F (825°C) and 150 psi. Steam is fed to the bottom of the reactor, both to fluidize the solids and to supply hydrogen through the steam carbon reactor. The 1850°F (1000°C) calcined dolomite or limestone acceptor showers into the top of the reactor, falling countercurrent to the rising gas. The acceptor is collected in a boot at the bottom of the gasifier and is returned pneumatically to the regenerator. Char is withdrawn from the middle of the bed and also fed pneumatically to the regenerator.

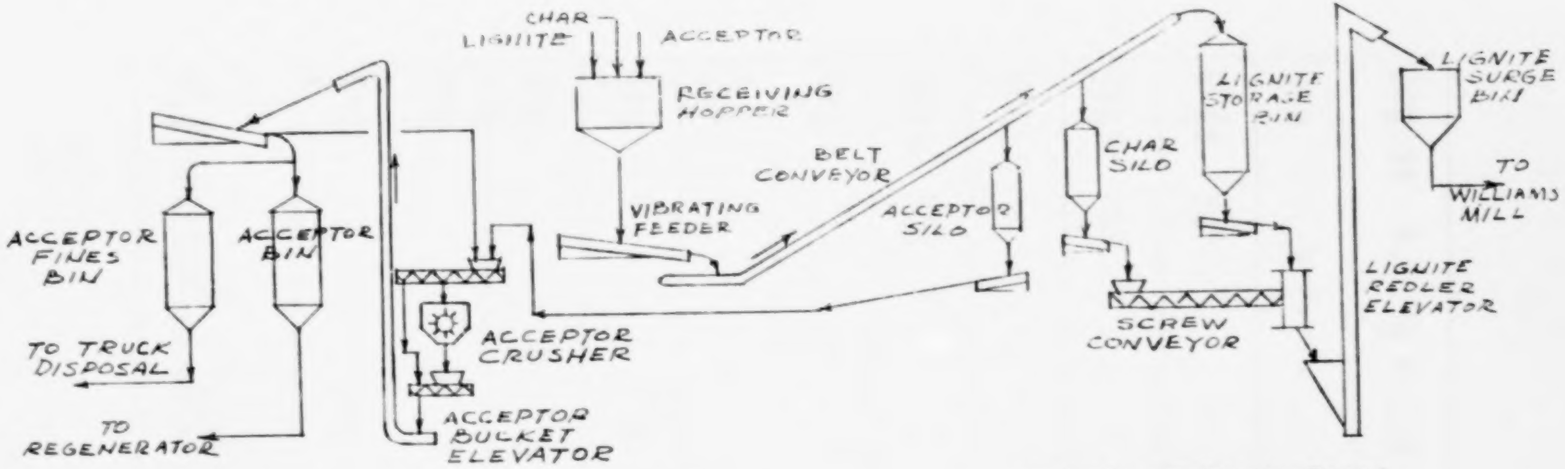
The heat for the gasification reaction is supplied in part by the hot acceptor but primarily by the chemical reaction between the calcined dolomite and carbon dioxide:

$$\underset{\text{calcined limestone}}{CaO} \quad + \quad \underset{\text{carbon dioxide}}{CO_2} \longrightarrow \underset{\text{limestone}}{CaCO_3} \quad + \text{ heat}$$

This reaction results in the production of more hydrogen by eliminating a large portion of the carbon dioxide and unbalancing the water gas shift reactor equilibrium to force the production of hydrogen. The limestone also reacts with the hydrogen sulfide in the system.

The regenerator is a single-stage, fluidized-bed vessel that operates at 1850°F (1000°C) and 148 psi. The crushed and sized dolomite (8x14 mesh) is fed to the regenerator through a lockhopper similar to that used to feed coal to the gasifier. Air is used to fluidize the bed and to burn the spent char to ash, thereby supplying the heat to reverse the caronation reaction and to heat the calcined dolomite. The calcined dolomite is transferred pneumatically to the gasifier. Ash is entrained with the hot combustion gas from the regenerator and cooled in a venturi scrubber.

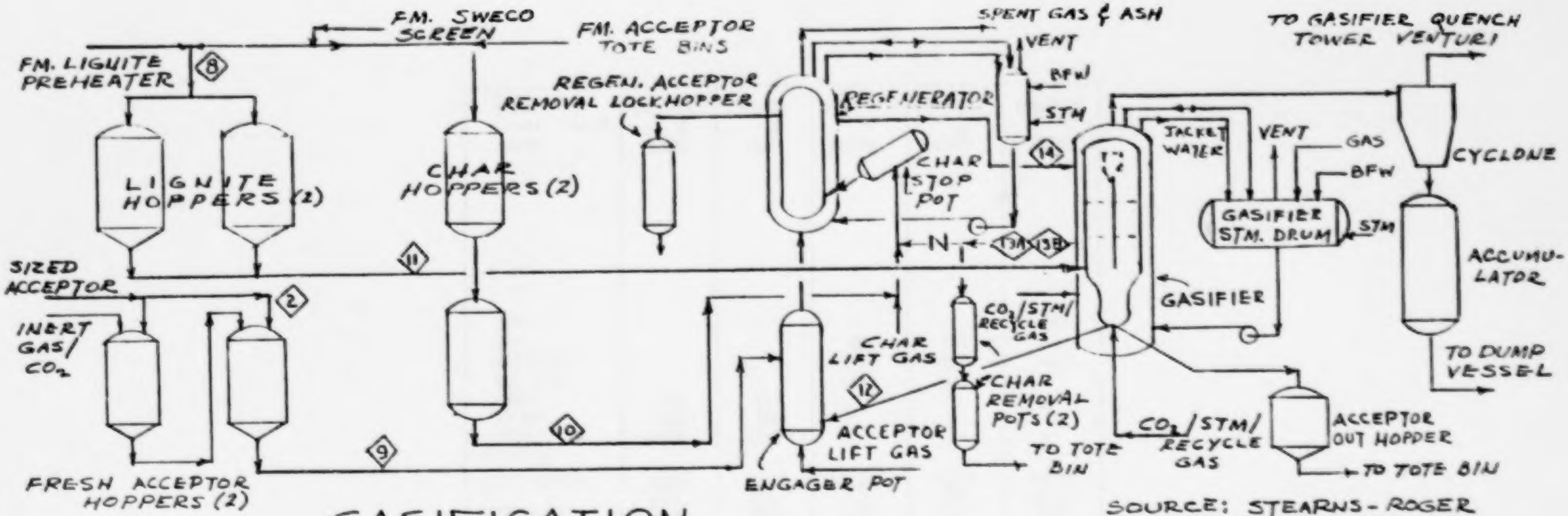
The downstream product gas system includes a water-venturi scrubber plus a dish-and-donut quench tower, no carbon monoxide shift unit, a Benfield gas purification unit, and a fixed-bed methanator employing a patented catalyst.


CHAR
LIGNITE
ACCEPTOR
RECEIVING HOPPER
VIBRATING FEEDER
BELT CONVEYOR
ACCEPTOR SILO
CHAR SILO
LIGNITE STORAGE BIN
LIGNITE SURGE BIN
TO WILLIAMS MILL
LIGNITE REDLER ELEVATOR
SCREW CONVEYOR
ACCEPTOR FINES BIN
ACCEPTOR BIN
TO TRUCK DISPOSAL
TO REGENERATOR
ACCEPTOR CRUSHER
ACCEPTOR BUCKET ELEVATOR

FEED PREPARATION
CO_2-ACCEPTOR PILOT PLANT

SOURCE: STEARNS-ROGER DRAWINGS OF 1976

MATERIAL BALANCE					
Stream Ident.	Raw Acceptor	Sized Acceptor	Raw Coal	Coal Feed and Oversize	Char
Stream No.	◇1	◇2	◇3	◇4	◇5
Rate, lbs/hr	72000	8795	12769	12769	60000
Analysis					
$CaCO_3$	70200	8575	-	-	-
$MgCO_3$	864	106	-	-	-
Other	936	114	-	-	-
MAF Coal	-	-	7719	7719	-
Moisture	-	-	4469	4469	6000
Ash	-	-	581	581	-
Char	-	-	-	-	54000
Total	72000	8795	12769	12769	60000
Press., psig	0	0	0	0	0
Temp., °F	Ambient	Ambient	Ambient	Ambient	Ambient

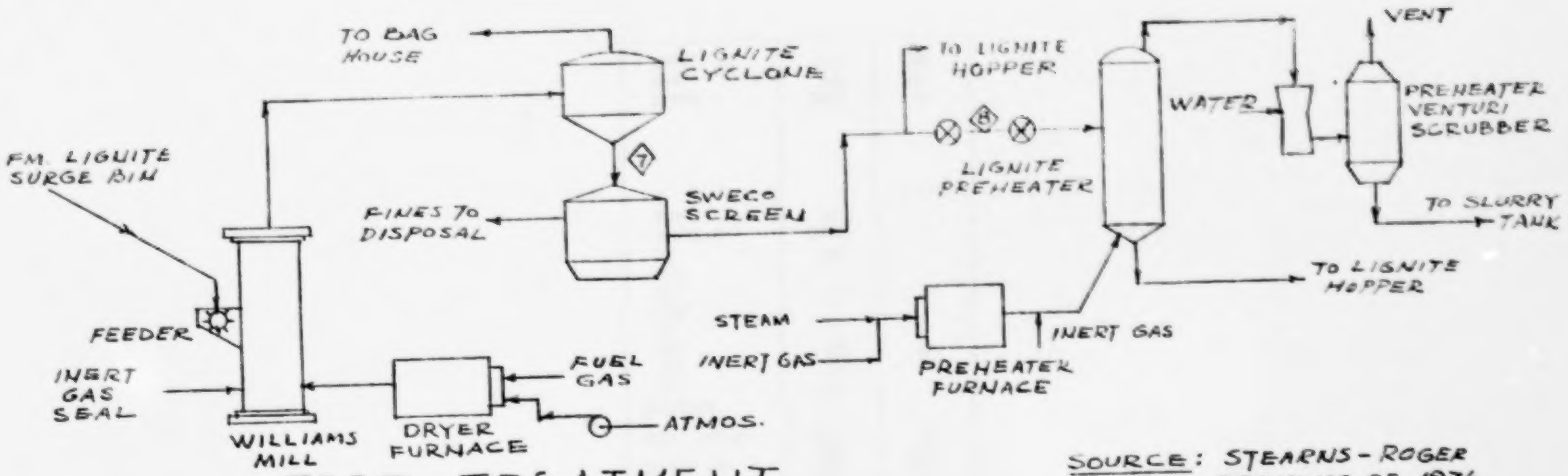

FM. LIGUITE PREHEATER
8
FM. SWECO SCREEN
FM. ACCEPTOR TOTE BINS
SPENT GAS & ASH
VENT
BFW
STM
TO GASIFIER QUENCH TOWER VENTURI
LIGNITE HOPPERS (2)
CHAR HOPPERS (2)
REGEN. ACCEPTOR REMOVAL LOCKHOPPER
REGENERATOR
CHAR STOP POT
14
JACKET WATER
VENT
GAS
BFW
CYCLONE
GASIFIER STM. DRUM
STM
ACCUMULATOR
N
13A
13B
11
SIZED ACCEPTOR
2
INERT GAS/ CO_2
GASIFIER
TO DUMP VESSEL
CO_2/STM/ RECYCLE GAS
CHAR LIFT GAS
12
CHAR REMOVAL POTS (2)
10
9
ACCEPTOR LIFT GAS
TO TOTE BIN
CO_2/STM/ RECYCLE GAS
ACCEPTOR OUT HOPPER
TO TOTE BIN
FRESH ACCEPTOR HOPPERS (2)
ENGAGER POT

GASIFICATION

CO_2 - ACCEPTOR PILOT PLANT

SOURCE: STEARNS - ROGER DRAWINGS OF 1976.

MATERIAL BALANCE												
Stream Ident.	Sized Acceptor	Sized Char	Coal to Preheater	Sized Acceptor	Sized Char	Coal to Gasifier	Recarb Acceptor	Fuel Char from Gasifier to Regenerator	Acceptor in Fuel Char from Gasifier to Regenerator	Calcined Acceptor	Gasifier Overhead Solids Withdrawal	Gasifier Overhead Gas
Stream No.	2	6	8	9	10	11	12	13A	13B	14	15	16
Rate, lbs/hr	8795	5000	4211	600	46	2874	12000	817	1800	10450	105	3425
Analysis												
Moisture	-	100	211	-	1	144	-	-	-	-	-	1180
$CaCO_3$	8575	-	-	585	-	-	-	-	-	-	-	-
$MgCO_3$	106	-	-	7.2	-	-	-	-	-	-	-	-
Other	114	-	-	7.8	-	-	-	-	-	-	-	-
MAF Char	-	4900	-	-	45	-	-	-	-	-	71	25
C	-	-	4000	-	-	2730	-	817	-	-	-	-
H_2	-	-	-	-	-	-	-	-	-	-	1	1319
N_2	-	-	-	-	-	-	-	-	-	-	-	75
S Total	-	-	-	-	-	-	24	-	2	21	Trace	-
Ash	-	-	-	-	-	-	-	-	-	-	7	-
O_2	-	-	-	-	-	-	-	-	-	-	26	-
CO_2	-	-	-	-	-	-	1080	-	715	84	-	224
CaO	-	-	-	-	-	-	9120	-	911	8777	-	-
MgO	-	-	-	-	-	-	324	-	32	387	-	-
CH_4	-	-	-	-	-	-	-	-	-	-	-	306
CO	-	-	-	-	-	-	-	-	-	-	-	296
Inert	-	-	-	-	-	-	1452	-	140	1181	-	-
Total	8795	5000	4211	600	46	2874	12000	817	1800	10450	105	3425
Press., psig	0	0	0	168	156	155	168	150	150	149	148	148
Temp., °F	Ambient	125	100	Ambient	Ambient	300	1450	1450	1450	1800	450	450


TO BAG HOUSE
LIGNITE CYCLONE
7
FM. LIGNITE SURGE BIN
FEEDER
INERT GAS SEAL
WILLIAMS MILL
FINES TO DISPOSAL
SWECO SCREEN
DRYER FURNACE
FUEL GAS
ATMOS.
TO LIGNITE HOPPER
8
LIGNITE PREHEATER
STEAM
INERT GAS
PREHEATER FURNACE
INERT GAS
WATER
VENT
PREHEATER VENTURI SCRUBBER
TO SLURRY TANK
TO LIGNITE HOPPER

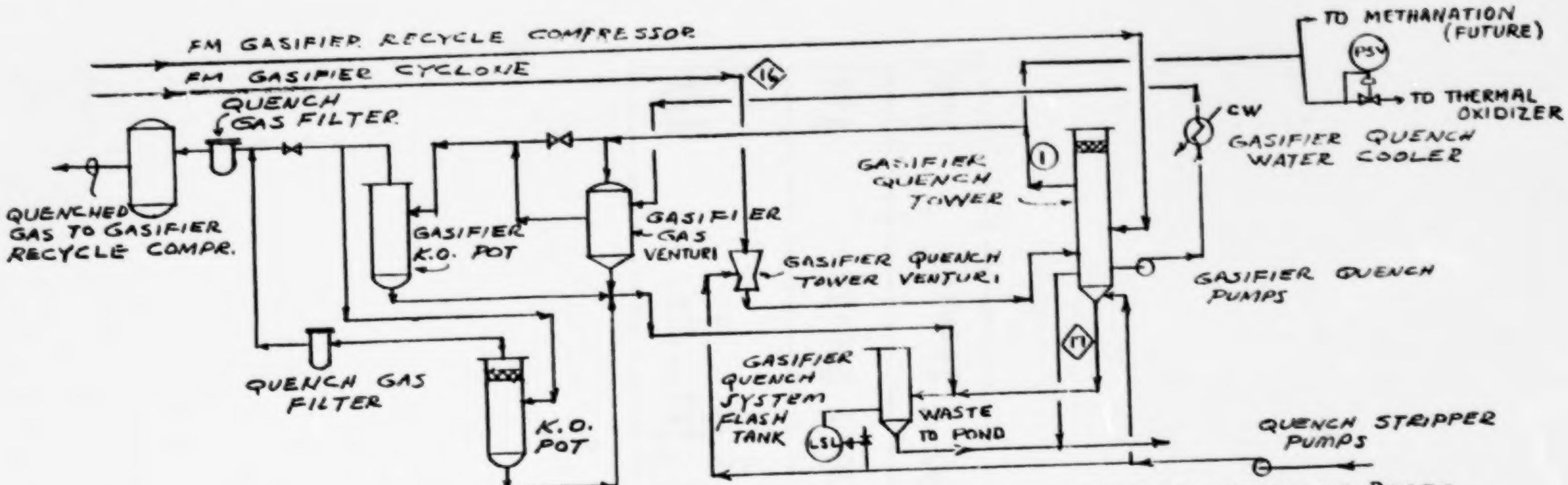
SOURCE: STEARNS - ROGER DRAWINGS OF 1976.

FEED TREATMENT

CO_2 - ACCEPTOR PILOT PLANT

MATERIAL BALANCE

Stream Ident.	Coal from Cyclone	Coal to Preheater
Stream No.	7	8
Rate, lbs/hr	5684	4211
Analysis		
Moisture	284	211
Char	-	-
C	3564	2640
H_2	243	180
N_2	27	20
S Total	27	20
Ash	378	280
O_2	1161	860
Total	5684	4211
Press., psig	0	0
Temp., °F	200	100

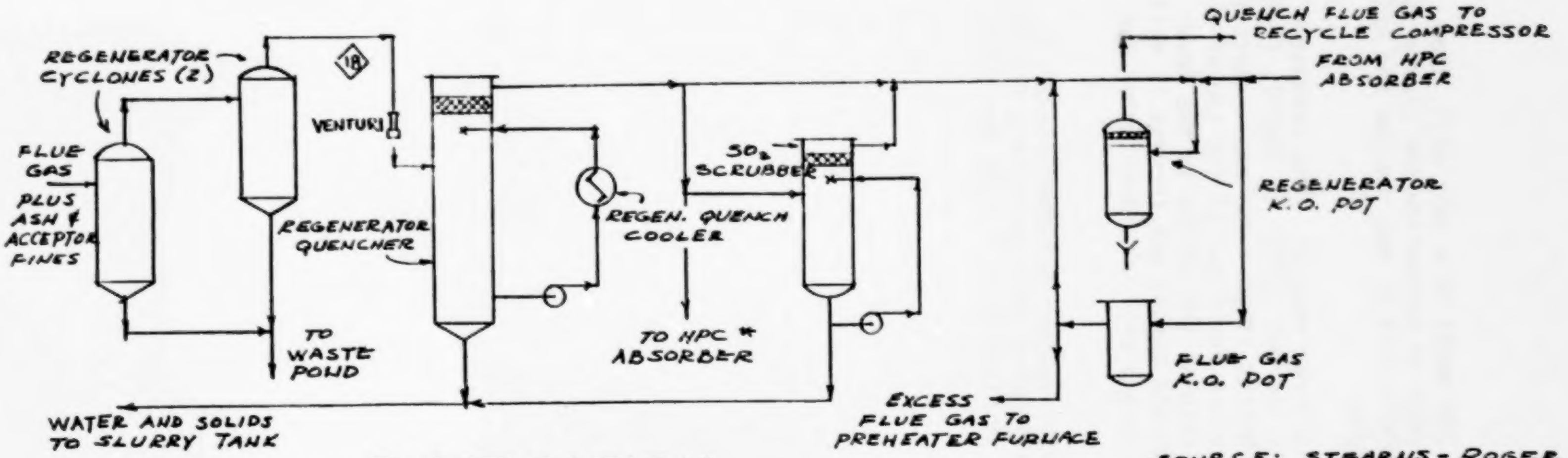

FM GASIFIER RECYCLE COMPRESSOR
FM GASIFIER CYCLONE
16
TO METHANATION (FUTURE)
PSV
TO THERMAL OXIDIZER
QUENCH GAS FILTER
CW
GASIFIER QUENCH WATER COOLER
1
GASIFIER QUENCH TOWER
QUENCHED GAS TO GASIFIER RECYCLE COMPR.
GASIFIER K.O. POT
GASIFIER GAS VENTURI
GASIFIER QUENCH TOWER VENTURI
GASIFIER QUENCH PUMPS
17
QUENCH GAS FILTER
K.O. POT
GASIFIER QUENCH SYSTEM FLASH TANK
LSL
WASTE TO POND
QUENCH STRIPPER PUMPS

SOURCE: STEARNS ROGER DRAWINGS OF 1976.

GAS PURIFICATION
CO_2 - ACCEPTOR PILOT PLANT

MATERIAL BALANCE		
Stream Ident.	Gasifier Overhead Gas	Solids in Quench Tower Water
Stream No.	16	17
Rate, lbs/hr	3425	37
Analysis		
H_2	1319	1
CO_2	224	-
CH_4	306	11
O_2	-	-
C_2H_6	-	-
N_2	75	-
H_2O	-	-
CO	296	-
Moisture	1180	-
Char	25	-
S	-	Trace
Total	3425	37
Press., psig	148	146
Temp., °F	450	120

① Approximately 25% of the gasifier quench tower product is used for controlling the system pressure. The balance is directed to the thermal oxidizer or the methanator, as conditions warrant.


REGENERATOR CYCLONES (2)
FLUE GAS PLUS ASH & ACCEPTOR FINES
18
VENTURI
REGENERATOR QUENCHER
REGEN. QUENCH COOLER
TO HPC * ABSORBER
SO_2 SCRUBBER
TO WASTE POND
WATER AND SOLIDS TO SLURRY TANK
EXCESS FLUE GAS TO PREHEATER FURNACE
QUENCH FLUE GAS TO RECYCLE COMPRESSOR
FROM HPC ABSORBER
REGENERATOR K.O. POT
FLUE GAS K.O. POT

SOURCE: STEARNS - ROGER DRAWINGS

PURIFICATION

CO_2 - ACCEPTOR PILOT PLANT

MATERIAL BALANCE	
Stream Ident.	Flue Gas from Regenerator
Stream No.	18
Rate, lbs/hr	10178
Analysis	
H_2	20
CO_2	2840
CH_4	-
O_2	-
C_2H_6	-
N_2	7175
H_2O	-
CO	143
Light Oil	-
Middle Oil	-
Heavy Oil	-
H_2S	Trace
Total	10178
Press., psig	146
Temp., °F	775

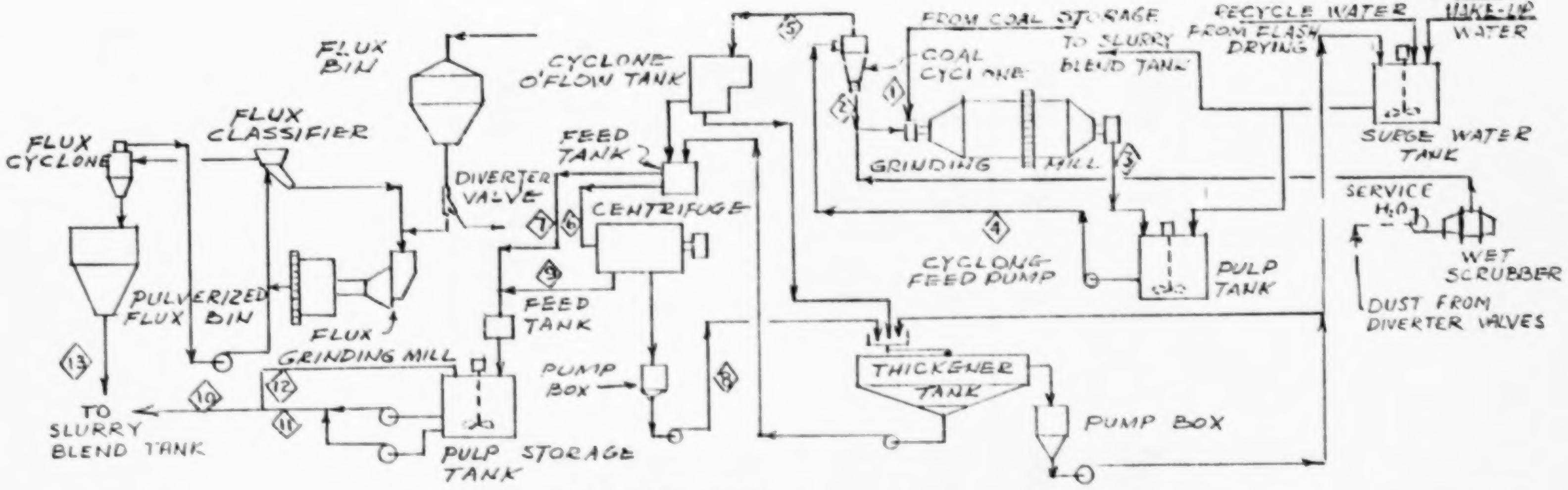
* HPC - 3 HYDROXY-2-PHENYLCINCHONINIC ACID

BI-GAS

Coal is crushed to 0.003-inch diameter (minus 200 mesh) in a roll mill, then mixed into a water slurry. A triplex pump is used to pressurize the slurry to 1500 psig. A preheater heats the slurry to 1000°F (538°C) and the gas and solids are separated in a flash tank-cyclone combination.

The gasifier is a vertical, two-stage, fast-fluid-bed reactor. The preheated coal is fed to the top stage, where it contacts the hot (2700° to 3000°F, [1480° -1650°C]) hydrogen-rich producer gas from the bottom stage. The coal reacts to form a methane-rich gas and char. Gas and char are swept out of the top of the reactor at 1700°F (925°C) to a cyclone, which returns the solids to the lower stage reactor. The char is gasified with steam and oxygen and the ash is melted. The resulting slag falls from the lower stage into a pool of quench water and is removed from the reactor.

Downstream processes include a conventional water-venturi scrubber-cooler, a carbon monoxide shift unit, a Selexol gas purification unit and both a fluidized bed and a conventional packed-bed methanator. A Claus unit is used for sulfur removal.


FLUX BIN
FLUX CYCLONE
FLUX CLASSIFIER
PULVERIZED FLUX BIN
FLUX GRINDING MILL
13
TO SLURRY BLEND TANK
10
12
11
DIVERTER VALVE
CYCLONE O'FLOW TANK
5
FEED TANK 2
7
6
CENTRIFUGE
9
FEED TANK
PUMP BOX
8
PULP STORAGE TANK
FROM COAL STORAGE
TO SLURRY BLEND TANK
COAL CYCLONE
1
2
GRINDING MILL
3
4
CYCLONE FEED PUMP
PULP TANK
THICKENER TANK
PUMP BOX
RECYCLE WATER FROM FLASH DRYING
MAKE-UP WATER
SURGE WATER TANK
SERVICE H_2O
WET SCRUBBER
DUST FROM DIVERTER VALVES

COAL HANDLING

BCR BI-GAS PILOT PLANT

SOURCE: STEARNS-ROGER CORP DWG 22221, SHEET 00-1-001, 11/13/73.

MATERIAL BALANCE

Stream Ident.	Coal from Storage	Coal from Cyclone	Coal from Grinding Mill	Coal from Pulp Tank	Coal from Coal Cyclone	Coal to Centrifuge	Centrifuge Coal Bypass	Coal-Centrifuge to Thickener	Coal-Centrifuge to Pulp Tank	Coal to Slurry Blend Tank	Coal from Pulp Storage	Coal Recycle Pulp Storage	Flux to Pulverized Flux Bin
Stream No.	1	2	3	4	5	6	7	8	9	10	11	12	13
Rate, lbs/hr	15000	38000	38000	94000	56000	52000	4000	34400	17600	27600	15600	128400	1100*
Analysis													
H_2	-	-	-	-	-	-	-	-	-	-	-	-	-
CO_2	-	-	-	-	-	-	-	-	-	-	-	-	-
CH_4	-	-	-	-	-	-	-	-	-	-	-	-	-
O_2	-	-	-	-	-	-	-	-	-	-	-	-	-
C_2H_6	-	-	-	-	-	-	-	-	-	-	-	-	-
N_2	-	-	-	-	-	-	-	-	-	-	-	-	-
H_2O	1000	19000	19000	61000	42000	39000	3000	33400	5600	17800	69200	51400	-
CO	-	-	-	-	-	-	-	-	-	-	-	-	-
Light Oil	-	-	-	-	-	-	-	-	-	-	-	-	-
Middle Oil	-	-	-	-	-	-	-	-	-	-	-	-	-
Heavy Oil	-	-	-	-	-	-	-	-	-	-	-	-	-
Coal	14000	19000	19000	33000	14000	13000	1000	1000	12000	9097	86800	77000	-
Flux	-	-	-	-	-	-	-	-	-	-	-	-	1100
Ash	-	-	-	-	-	-	-	-	-	703	-	-	-
Total	15000	38000	38000	94000	56000	52000	4000	34400	17600	27600	156000	128400	1100
Press., psig	Atmos.	Atmos.	Atmos.	Atmos.	Atmos.	Atmos.	Atmos.	Atmos.	Atmos.	25	Atmos.	Atmos.	Atmos.
Temp., °F	Ambient	Ambient	Ambient	Ambient	Ambient	Ambient	Ambient	Ambient	Ambient	60	Ambient	Ambient	Ambient

*ESTIMATED NORMAL ADDITION RATE WHEN REQUIRED.

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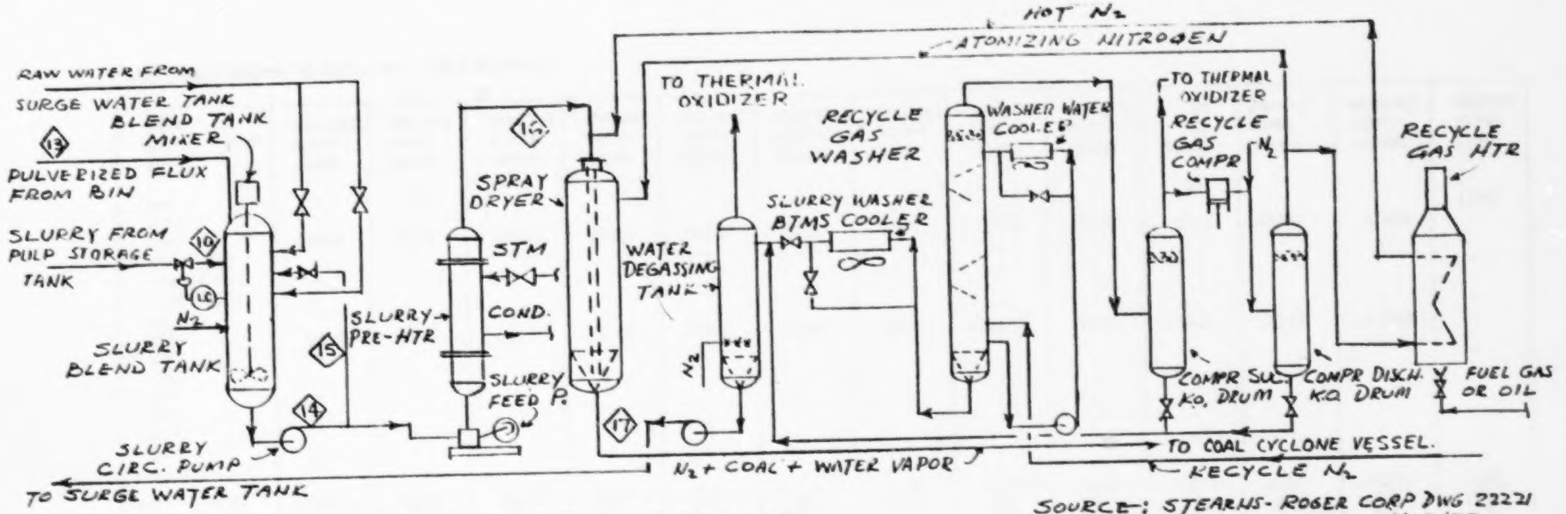
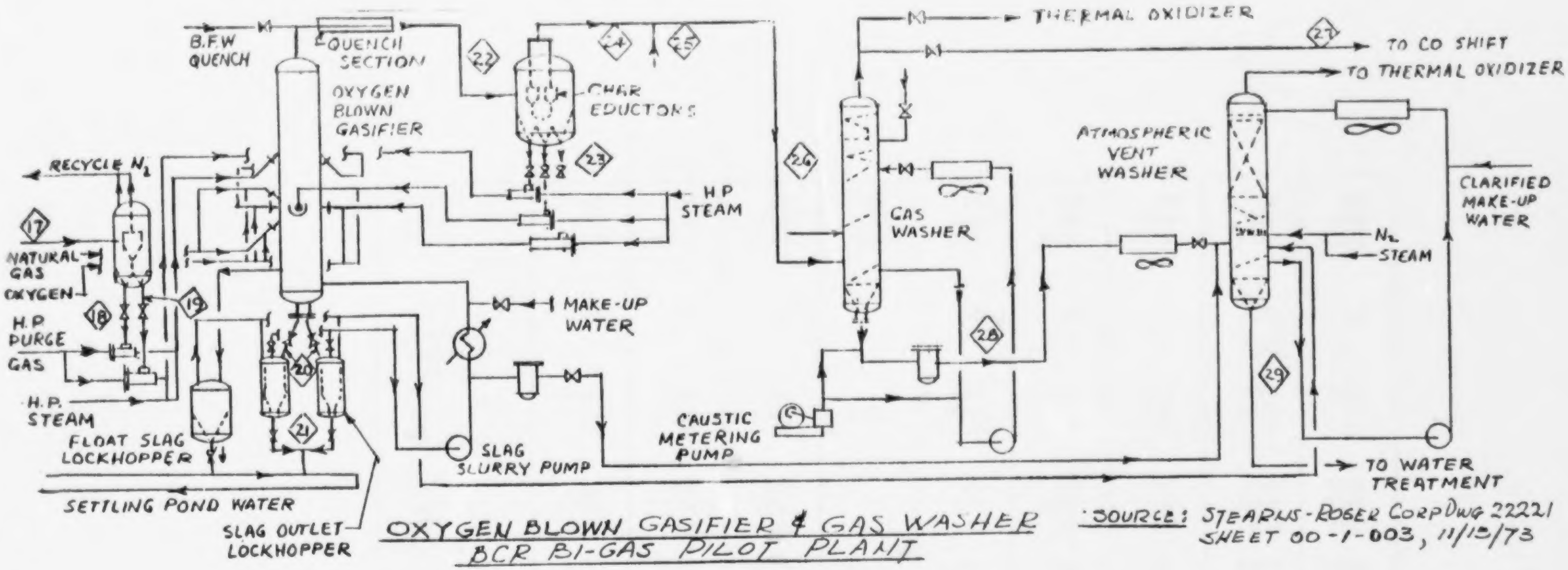

HOT N2
ATOMIZING NITROGEN
RAW WATER FROM SURGE WATER TANK
BLEND TANK MIXER
13
PULVERIZED FLUX FROM BIN
SLURRY FROM PULP STORAGE TANK
10
LC
N2
SLURRY BLEND TANK
15
14
SLURRY CIRC. PUMP
TO SURGE WATER TANK
SLURRY PRE-HTR
16
SPRAY DRYER
STM
COND.
SLURRY FEED P.
17
N2 + COAL + WATER VAPOR
TO THERMAL OXIDIZER
WATER DEGASSING TANK
N2
SLURRY WASHER BTMS COOLER
RECYCLE GAS WASHER
WASHER WATER COOLER
TO THERMAL OXIDIZER
RECYCLE GAS COMPR
N2
COMPR SUC KO. DRUM
COMPR DISCH KO DRUM
RECYCLE GAS HTR
FUEL GAS OR OIL
TO COAL CYCLONE VESSEL.
RECYCLE N2

SOURCE: STEARNS-ROGER CORP DWG 22221 SHEET 00-1-002, 11/15/73.

SLURRY FEED DRYING
BCR BI-GAS PILOT PLANT

MATERIAL BALANCE						
Stream Ident.	Coal to Slurry Blend Tank	Flux to Pulverized Flux Bin	Coal to Slurry Circ. Pumps	Coal Slurry Recircu-lating Stream	Coal Slurry thru Pre-heater to Spray Drier	N₂-Coal to Coal Cyclone
Stream No.	10	13	14	15	16	17
Rate, lbs/hr	27600	0000	46032	18432	27600	251300
Analysis						
H_2	-	-	-	-	-	-
CO_2	-	-	-	-	-	-
CH_4	-	-	-	-	-	-
O_2	-	-	-	-	-	-
C_2H_6	-	-	-	-	-	-
N_2	-	-	-	-	-	223700
H_2O	17800	-	29700	11900	17800	17800
CO	-	-	-	-	-	-
Light Oil	-	-	-	-	-	-
Middle Oil	-	-	-	-	-	-
Heavy Oil	-	-	-	-	-	-
Coal Ash Free	9097	-	15160	6063	9097	9097
Ash	703	0000	1172	469	703	703
Total	27600	0000	46032	18432	27600	251300
Press., psig	25	Atmos.	5	80	1175	1210
Temp., °F	60	Ambient	60	60	475	550


B.F.W QUENCH
QUENCH SECTION
OXYGEN BLOWN GASIFIER
CHAR EDUCTORS
22
23
24
25
RECYCLE N_2
17
NATURAL GAS
OXYGEN
18
19
H.P PURGE GAS
H.P. STEAM
H P STEAM
FLOAT SLAG LOCKHOPPER
20
21
SETTLING POND WATER
SLAG OUTLET LOCKHOPPER
MAKE-UP WATER
SLAG SLURRY PUMP
CAUSTIC METERING PUMP
26
GAS WASHER
28
THERMAL OXIDIZER
27
TO CO SHIFT
TO THERMAL OXIDIZER
ATMOSPHERIC VENT WASHER
N_2
STEAM
CLARIFIED MAKE-UP WATER
29
TO WATER TREATMENT

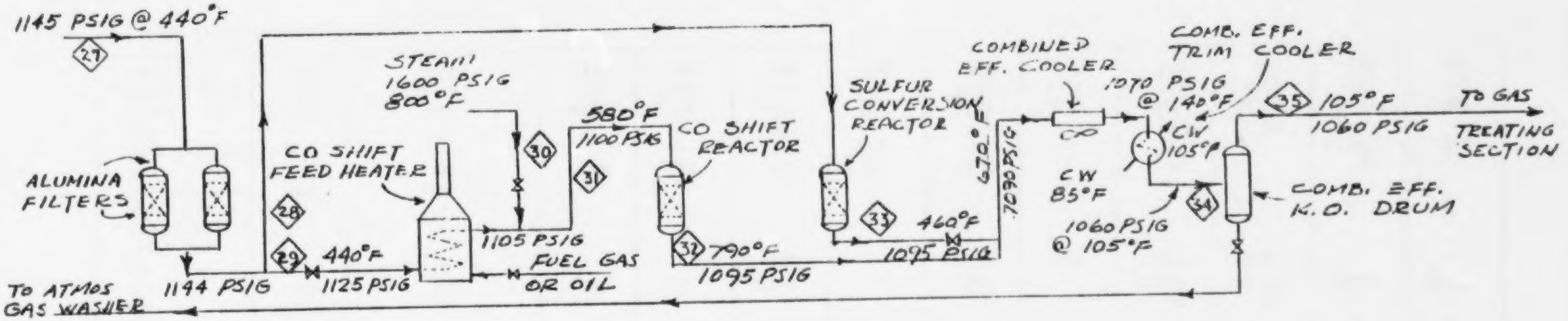
OXYGEN BLOWN GASIFIER & GAS WASHER
BCR BI-GAS PILOT PLANT

SOURCE: STEARNS-ROGER CORP DWG 22221
SHEET 00-1-003, 11/13/73

MATERIAL BALANCE

Stream Ident.	N_2-Coal to Coal Cyclone	(Each) Slurry to Gasifier Upper Stage	(Each) Slurry to Slag Outlet Hoppers	(Each) Slag Slurry to Pond	Raw Gas from Gasifier	(Each Leg) Char to Gasifier	Raw Gas from Cyclone	Recycled Purge Gas	Gas to Washer	Scrubbed Raw Gas	Char Slurry to Atmospheric Vent Gas Washer	Char Slurry to Water Treatment
Stream No.	17	18 19	20*	21*	22	23	24	25	26	27	28	29
Rate, lbs/hr	251300	5001	40668	1725	54811	3126	45431	2042	47473	36490	10983	10983
Analysis												
H_2	-	-	-	-	937	-	937	88	1025	1025	-	-
CO_2	-	-	-	-	10762	-	10762	1068	11830	11830	-	-
CH_4	-	-	-	-	1649	-	1649	146	1795	1795	-	-
O_2	-	-	-	-	-	-	-	-	-	-	-	-
C_2H_6	-	-	-	-	-	-	-	-	-	-	-	-
N_2	223700	-	-	-	62	-	62	-	62	62	-	-
H_2O	17800	100	40000	1057	22001	-	22001	-	22001	11313	10688	10688
CO	-	-	-	-	9442	-	9442	740	10182	10182	-	-
Light Oil	-	-	-	-	-	-	-	-	-	-	-	-
Middle Oil	-	-	-	-	-	-	-	-	-	-	-	-
Heavy Oil	-	-	-	-	-	-	-	-	-	-	-	-
Coal Ash Free	9097	4549	-	-	-	-	-	-	-	-	-	-
Ash	703	352	668	668	1152	372	435	-	35	-	35	35
Char Ash Free	-	-	-	-	8523	2754	260	-	260	-	260	260
H_2S	-	-	-	-	283	-	283	-	283	283	-	-
Total	251300	5001	40668	1725	54811	3126	45431	2042	47473	36490	10983	10983
Press., psig	1210	1175	1150	1150	1150	1145	1145	1145	1145	1145	1145	10
Temp., °F	550	475	170	170	800	800	800	100	600	440	440	150

*These lines operate alternately.

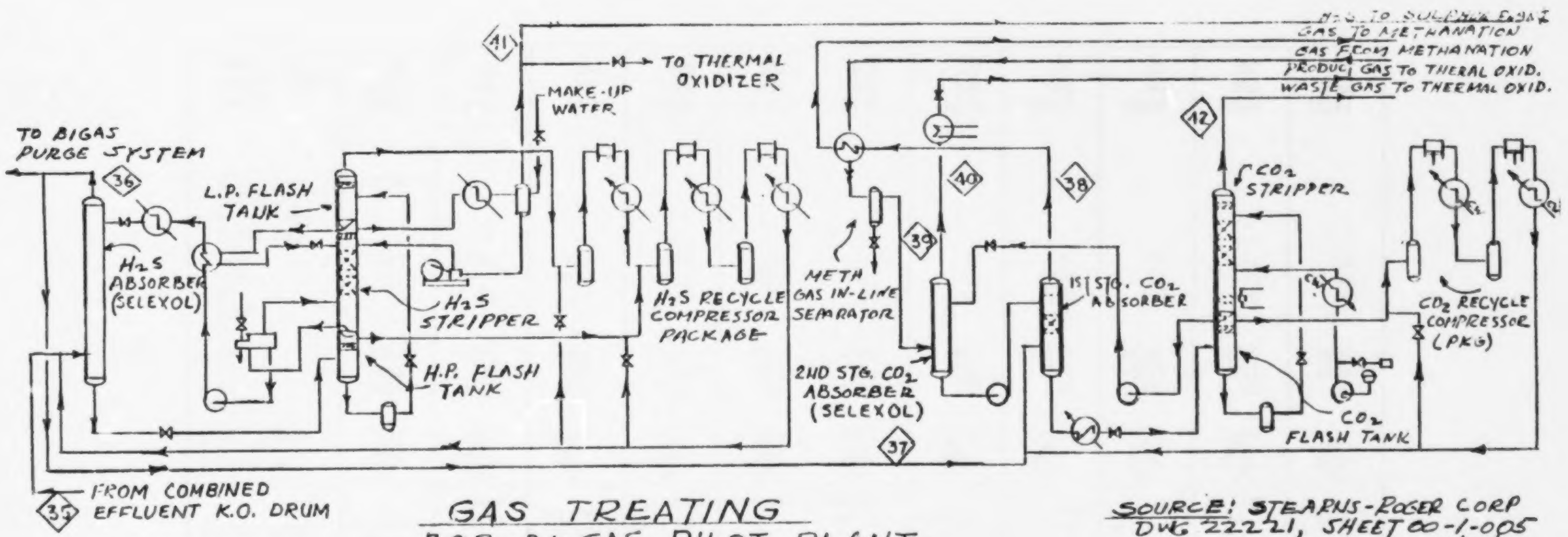


1145 PSIG @ 440°F
27
ALUMINA FILTERS
TO ATMOS GAS WASHER
1144 PSIG
28
29
440°F
1125 PSIG
CO SHIFT FEED HEATER
STEAM 1600 PSIG 800°F
30
1105 PSIG
FUEL GAS OR OIL
580°F
1100 PSIG
31
CO SHIFT REACTOR
32
790°F
1095 PSIG
SULFUR CONVERSION REACTOR
33
460°F
1095 PSIG
670°F
1070 PSIG
COMBINED EFF. COOLER
CW 85°F
1070 PSIG @ 140°F
COMB. EFF. TRIM COOLER
CW 105°F
1060 PSIG @ 105°F
34
COMB. EFF. K.O. DRUM
35
105°F
1060 PSIG
TO GAS TREATING SECTION

SOURCE: STEARNS-ROGER CORP DWG 22221
SHEET 00-1-004, 11/15/73.

CO SHIFT SECTION
BCI BI-GAS PILOT PLANT

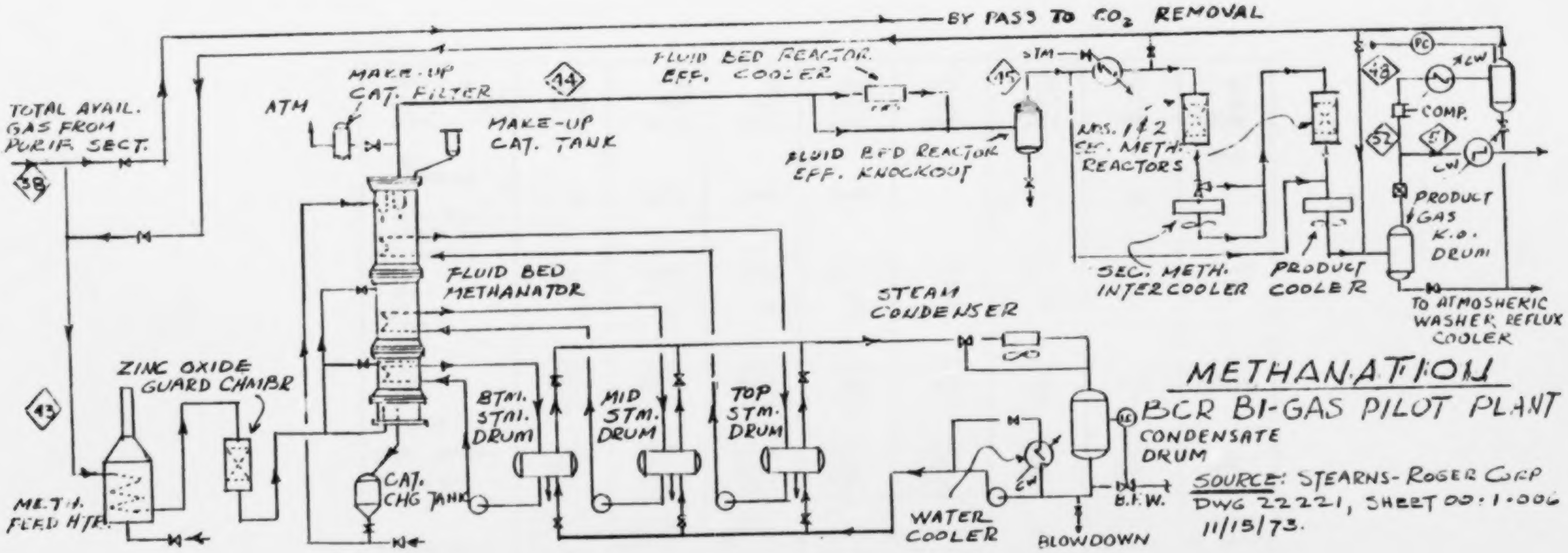
MATERIAL BALANCE									
Stream Ident.	Scrubbed Raw Gas	Sulfur Conversion Feed to Reactor	Shift Converter Gas Feed	Shift Converter Steam Feed	Shift Converter Total Feed	Shift Converter Reactor Effluent	Sulfur Conversion Reactor Effluent	Combined Effluent Gas to K.O. Drum	Cooled Gas to Gas Treating Section
Stream No.	27	28	29	30	31	32	33	34	35
Rate, lbs/hr	36490	17132	19358	6159	25517	25517	17132	42649	27757
Analysis									
H_2	1025	481	544	-	544	848	481	1328	1328
CO_2	11830	5554	6276	-	6276	12899	5554	18454	18314
CH_4	1795	842	953	-	953	953	842	1795	1795
O_2	-	-	-	-	-	-	-	-	-
C_2H_6	-	-	-	-	-	-	-	-	-
N_2	62	28	34	-	34	34	28	62	62
H_2O	11313	5318	5995	6159	12154	9443	5318	14761	23
CO	10182	4776	5406	-	5406	1190	4776	5966	5966
Light Oil	-	-	-	-	-	-	-	-	-
Middle Oil	-	-	-	-	-	-	-	-	-
Heavy Oil	-	-	-	-	-	-	-	-	-
H_2S	283	133	150	-	150	150	133	283	269
Total	36490	17132	19358	6159	25517	25517	17132	42649	27757
Press., psig	1145	1144	1144	1105	1105	1095	1144	1060	1060
Temp., °F	440	440	440	765	580	790	440	105	105


TO BIGAS PURGE SYSTEM
36
H_2S ABSORBER (SELEXOL)
L.P. FLASH TANK
H_2S STRIPPER
H.P. FLASH TANK
FROM COMBINED EFFLUENT K.O. DRUM
35
41
MAKE-UP WATER
TO THERMAL OXIDIZER
H_2S RECYCLE COMPRESSOR PACKAGE
METH GAS IN-LINE SEPARATOR
39
40
38
2ND STG. CO_2 ABSORBER (SELEXOL)
37
1ST STG. CO_2 ABSORBER
42
CO_2 STRIPPER
CO_2 FLASH TANK
CO_2 RECYCLE COMPRESSOR (PKG)
GAS TO METHANATION
GAS FROM METHANATION
PRODUCT GAS TO THERAL OXID.
WASTE GAS TO THERMAL OXID.

GAS TREATING
BCR BI-GAS PILOT PLANT

SOURCE: STEARNS-ROGER CORP
DWG 22221, SHEET 00-1-005
11/15/73

MATERIAL BALANCE								
Stream Ident.	Cooled Gas to Gas Treating Section	H_2S Absorber Gas Out	CO_2 Absorber Feed	Gas to Methanator	Gas from Methanator	Product Gas	H_2S to Sulfur Plant	Waste Gas to Thermal Oxidizer
Stream No.	35	36	37	38	39	40	41	42
Rate, lbs/hr	27757	26788	23591	9347	5998	4679	970	
Analysis								
H_2	1328	1331	1172	1170	42	42	-	2
CO_2	18314	17635	15531	598	576	66	678	15443
CH_4	1795	1795	1580	2316	5300	4504	-	59
O_2	-	-	-	-	-	-	-	-
C_2H_6	-	-	-	-	-	-	-	-
N_2	62	61	56	56	56	56	-	-
H_2O	23	-	-	-	13	-	23	20
CO	5966	5966	5252	5207	11	11	-	45
Light Oil	-	-	-	-	-	-	-	-
Middle Oil	-	-	-	-	-	-	-	-
Heavy Oil	-	-	-	-	-	-	-	-
H_2S	269	5ppm	5ppm	5ppm	-	-	269	-
Stripping Air	-	-	-	-	-	-	-	2619
Total	27757	26788	23591	9347	5998	4679	970	18188
Press., psig	1060	1036	1036	1016	925	915	20	20
Temp., °F	105	76	76	80	62	35	105	40

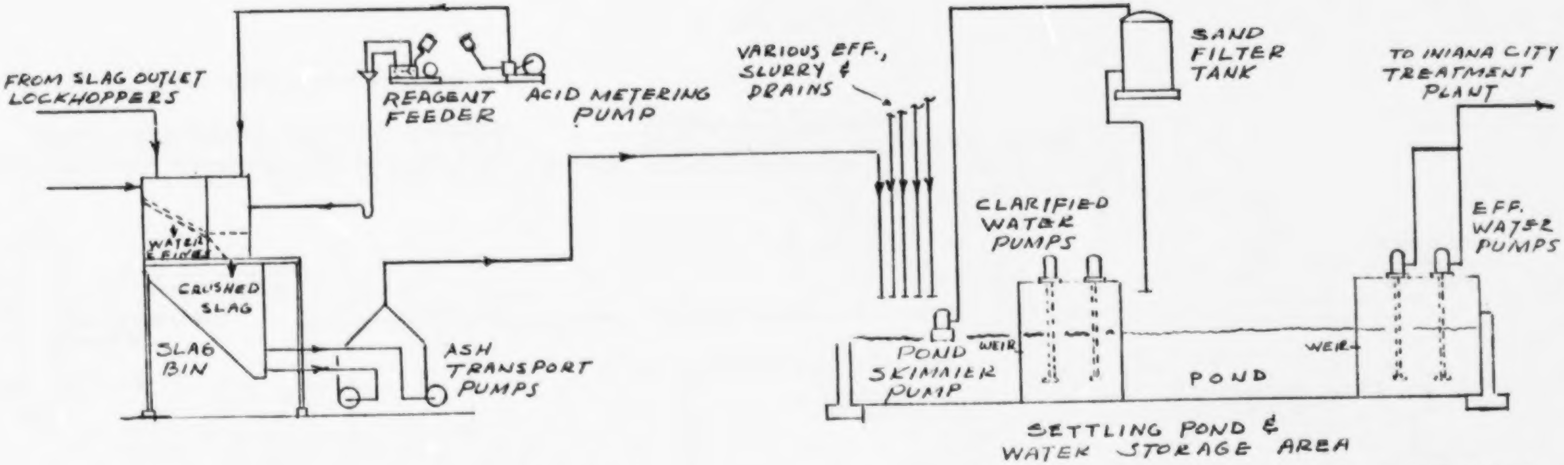

BY PASS TO CO2 REMOVAL
TOTAL AVAIL. GAS FROM PURIF. SECT.
38
ATM
MAKE-UP CAT. FILTER
MAKE-UP CAT. TANK
44
FLUID BED REACTOR EFF. COOLER
45
FLUID BED REACTOR EFF. KNOCKOUT
STM
NOS. 1 & 2 SEC. METH. REACTORS
SEC. METH. INTERCOOLER
PRODUCT COOLER
48
52
51
PC
CW
COMP.
PRODUCT GAS K.O. DRUM
TO ATMOSHERIC WASHER REFLUX COOLER
FLUID BED METHANATOR
STEAM CONDENSER
ZINC OXIDE GUARD CHMBR
43
METH. FEED HTR.
BTM. STM. DRUM
MID STM. DRUM
TOP STM. DRUM
CAT. CHG TANK
WATER COOLER
BLOWDOWN
B.F.W.
CONDENSATE DRUM

METHANATION
BCR BI-GAS PILOT PLANT

SOURCE: STEARNS-ROGER CORP
DWG 22221, SHEET 00:1-006
11/15/73.

MATERIAL BALANCE

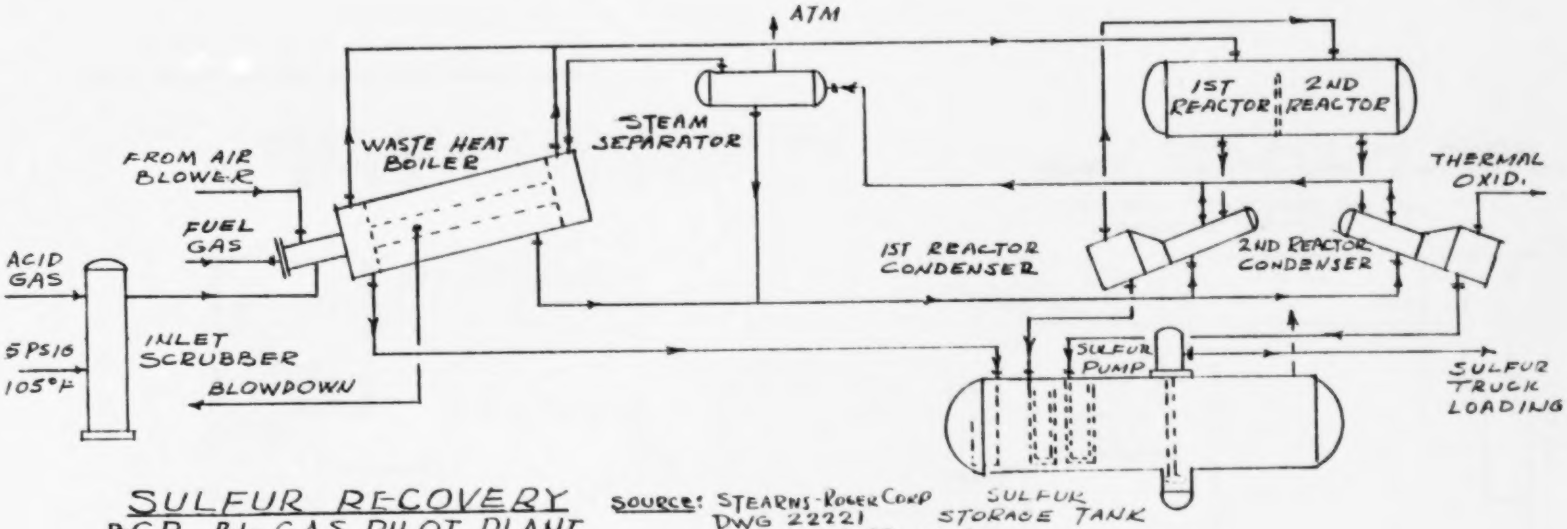
Stream Ident.	Gas to Methanator	Fluid Bed Methanator Total Feed	Fluid Bed Methanator Effluent	Fluid Bed Reactor Effluent K.O. Drum	Secondary Methanator Effluent No. 1 Reactor	Secondary Methanator Effluent No. 2 Reactor	Compressor Recycle	Total to Suction K.O. Drum	Effluent from Produce Gas K.O. Drum	Product Gas to Selexol	Gas to Recycle Compressor
Stream No.	38	43	44	45	46	47	48	49	50	51	52
Rate, lbs/hr	9347	9347	9347	9347	9347	9347	10732	20079	16739	5998	-
Analysis											
H_2	1170	1170	157	157	69	42	76	118	118	42	76
CO_2	598	598	598	598	577	577	1039	1616	1616	577	1039
CH_4	2316	2316	5000	5000	5229	5300	9492	14792	14792	5300	9492
O_2	-	-	-	-	-	-	-	-	-	-	-
C_2H_6	-	-	-	-	-	-	-	-	-	-	-
N_2	56	56	56	56	56	56	92	148	148	56	92
H_2O	-	-	3015	3015	3281	3361	13	3374	34	12	22
CO	5207	5207	521	521	135	11	20	31	31	11	20
Light Oil	-	-	-	-	-	-	-	-	-	-	-
Middle Oil	-	-	-	-	-	-	-	-	-	-	-
Heavy Oil	-	-	-	-	-	-	-	-	-	-	-
H_2S	5ppm	-	-	-	-	-	-	-	-	-	-
Total	9347	9347	9347	9347	9347	9347	10732	20079	16739	5998	10741
Press., psig	1016	998	970	960	945	935	935	930	930	925	925
Temp., °F	80	80	750	500	800	650	105	120	120	105	120


FROM SLAG OUTLET LOCKHOPPERS
WATER & FINES
CRUSHED SLAG
SLAG BIN
REAGENT FEEDER
ACID METERING PUMP
ASH TRANSPORT PUMPS
VARIOUS EFF., SLURRY & DRAINS
POND SKIMMER PUMP
WEIR
CLARIFIED WATER PUMPS
SAND FILTER TANK
POND
WEIR
EFF. WATER PUMPS
TO INIANA CITY TREATMENT PLANT
SETTLING POND & WATER STORAGE AREA

SLAG DISPOSAL
BCR BI-GAS PILOT PLANT

SOURCE: STEARNS-ROGER CORP DWG 22221 SHEET 00-1-29, 10/15/73.

Note: No data available to calculate material balance.


ATM
1ST REACTOR
2ND REACTOR
STEAM SEPARATOR
WASTE HEAT BOILER
FROM AIR BLOWER
FUEL GAS
ACID GAS
5 PSIG
105°F
INLET SCRUBBER
BLOWDOWN
THERMAL OXID.
1ST REACTOR CONDENSER
2ND REACTOR CONDENSER
SULFUR PUMP
SULFUR TRUCK LOADING
SULFUR STORAGE TANK

SULFUR RECOVERY
BCR BI-GAS PILOT PLANT

SOURCE: STEARNS-ROGER CORP
DWG 22221
SHEET 00-1-28, 10/15/73

Note: No data available to calculate material balances.

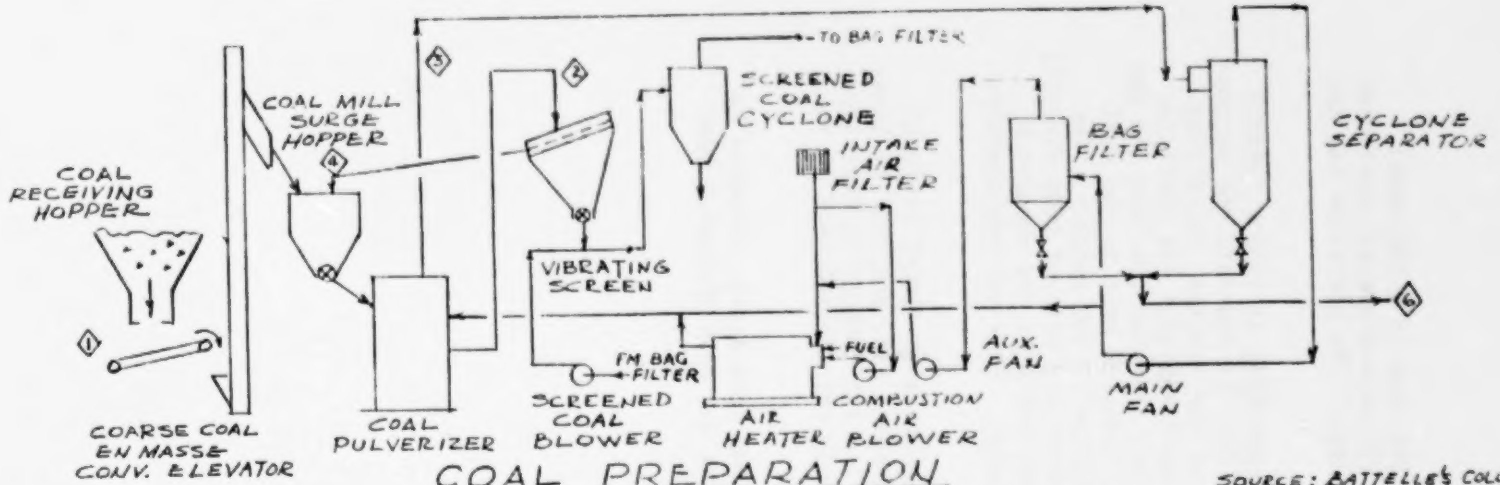
AGGLOMERATING BURNER

Coal is crushed to two different sizes, 0.09 x 0.006 inch (8 x 100 mesh) particles for the gasifier and 0.006-inch (minus 100 mesh-diameter) particles for the burner. Recirculating hot air dries the coal. The operation has two reactors — the gasifier and the burner.

The gasifier is a vertical, single-stage reactor operating at 1800°F (980°C) and 100 psig with an internal cyclone separator. Coal is fed into the reactor by lockhoppers, and steam is fed into the bottom of the reactor, fluidizing the coal bed. Hot agglomerates are formed when small residual ash particles are released from the coal and stick together. They are then fed into the top of the reactor, shower down through the coal bed, transfer heat to the coal gasification reaction, and are removed from the bottom of the reactor. The cyclone removes solids from the synthesis gas stream, and returns them directly to the coal bed via a standleg. Ash and excess agglomerates are removed by lockhopper from the bottom of the reactor to disposal. Char and agglomerates are removed and fed into the burner.

The burner is a vertical, single-stage reactor operating at 2100°F (1150°C). Char and ash agglomerates from the gasifier, compressed air, and coal by lockhopper are fed into the burner. The coal, char, and air combust to heat the recycling agglomerates. These are then continuously transferred back to the gasifier by a steam lift.

Off-gases from both units are passed through cyclone separators, scrubbed in a venturi, and thermally oxidized. Burner flue gas may pass through a heat exchanger and a gas turbine energy.

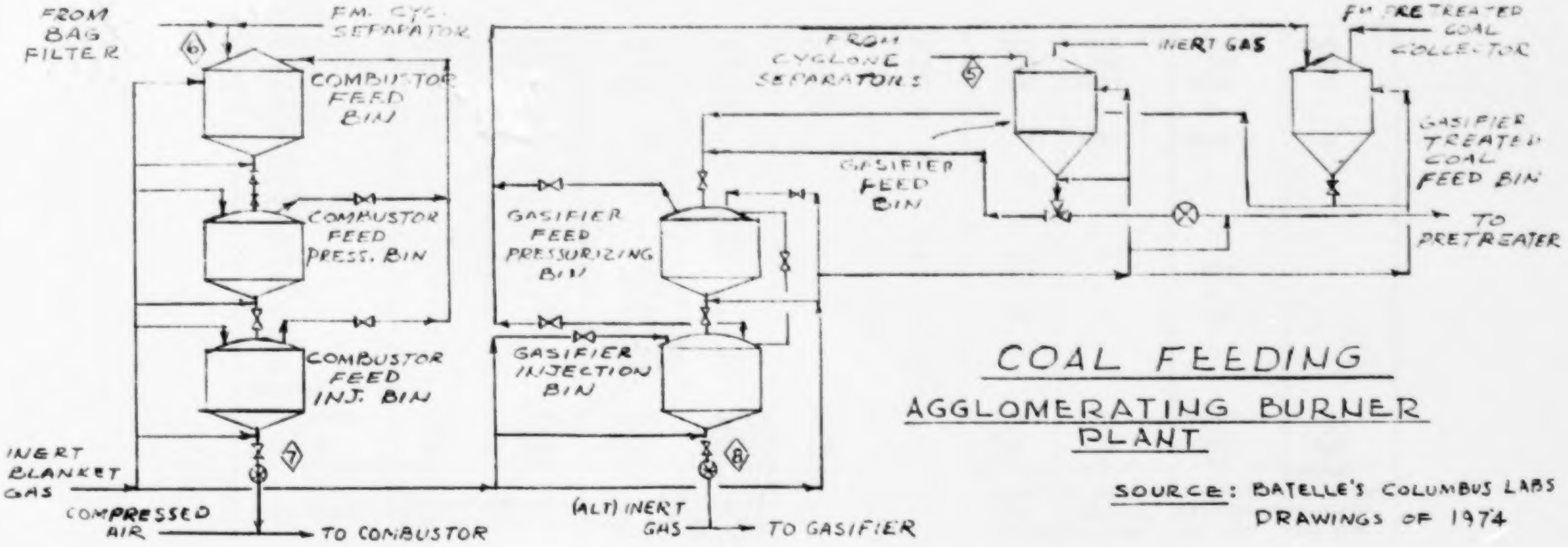

COAL RECEIVING HOPPER
1
COARSE COAL EN MASSE CONV. ELEVATOR
COAL MILL SURGE HOPPER
4
COAL PULVERIZER
5
2
VIBRATING SCREEN
SCREENED COAL BLOWER
FM BAG FILTER
SCREENED COAL CYCLONE
TO BAG FILTER
INTAKE AIR FILTER
AIR HEATER
FUEL
COMBUSTION AIR BLOWER
AUX. FAN
BAG FILTER
MAIN FAN
CYCLONE SEPARATOR
6

COAL PREPARATION

AGGLOMERATING BURNER PLANT

SOURCE: BATTELLE'S COLUMBUS LABS DRAWINGS OF 1974

MATERIAL BALANCE						
Stream Ident.	Incoming Coal	Pulverized Coal to Vibrating Screen	Pulverized Coal to Cyclone Separator	Oversized Coal to Coal Pulverizer	Screened Coal to Gasifier Feed Bin	Coal to Combuster Feed Bin
Stream No.	1	2	3	4	5	6
Rate, lbs/hr	10666	11600	4200	5800	5800	4200
Analysis						
H_2	-	-	-	-	-	-
CO_2	-	-	-	-	-	-
CH_4	-	-	-	-	-	-
O_2	-	-	-	-	-	-
C_2H_6	-	-	-	-	-	-
N_2	-	-	-	-	-	-
H_2O	-	-	-	-	-	-
CO	-	-	-	-	-	-
Light Oil	-	-	-	-	-	-
Middle Oil	-	-	-	-	-	-
Heavy Oil	-	-	-	-	-	-
Moisture	1066	464	168	232	232	168
MF Coal	9600	11136	4032	5568	5568	4032
Total	10000	11600	4200	5800	5800	4200
Press., psig	Atmos.	Atmos.	Atmos.	Atmos.	Atmos.	Atmos.
Temp., °F	Ambient	200	200	200	200	200

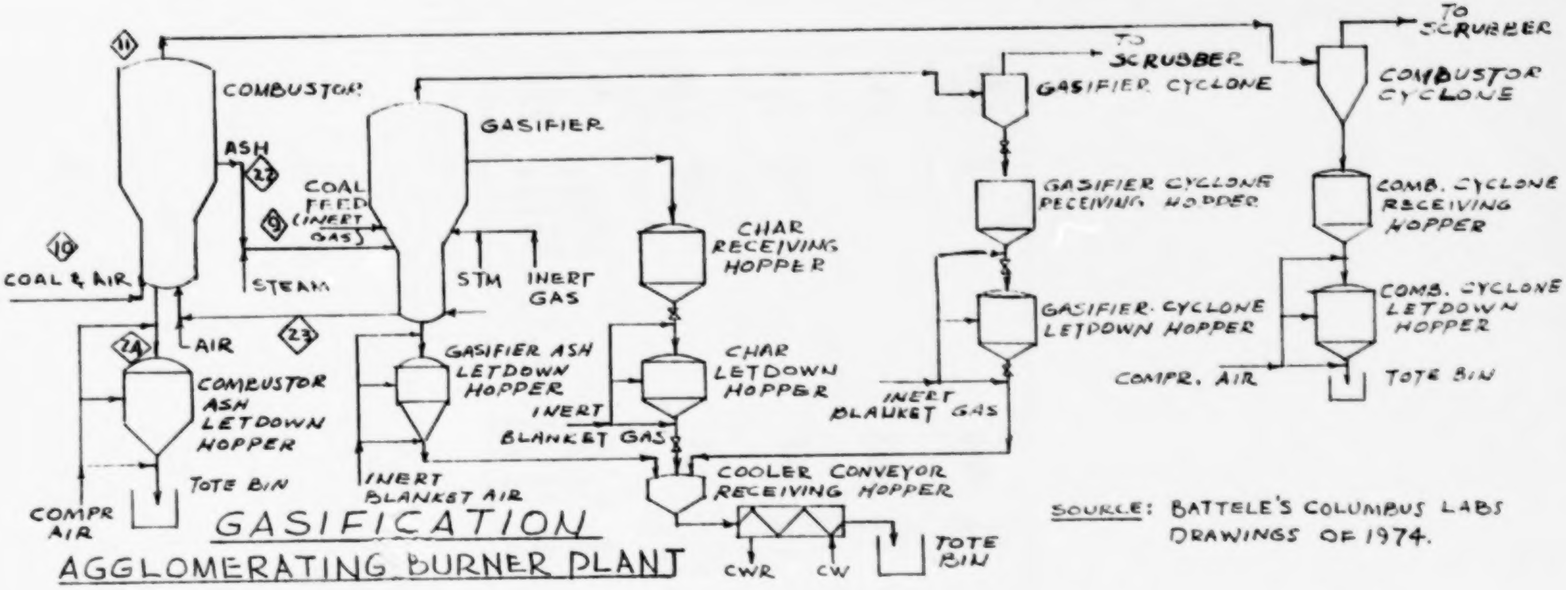

FROM BAG FILTER
6
FM. CYC. SEPARATOR
COMBUSTOR FEED BIN
COMBUSTOR FEED PRESS. BIN
COMBUSTOR FEED INJ. BIN
INERT BLANKET GAS
7
COMPRESSED AIR
TO COMBUSTOR
GASIFIER FEED PRESSURIZING BIN
GASIFIER INJECTION BIN
8
(ALT) INERT GAS
TO GASIFIER
FROM CYCLONE SEPARATORS
5
GASIFIER FEED BIN
INERT GAS
FM PRETREATED COAL COLLECTOR
GASIFIER TREATED COAL FEED BIN
TO PRETREATER

COAL FEEDING

AGGLOMERATING BURNER PLANT

SOURCE: BATELLE'S COLUMBUS LABS DRAWINGS OF 1974

MATERIAL BALANCE				
Stream Ident.	Screened Coal to Gasifier Feed Bin	Coal to Combuster Feed Bin	Coal to Combuster	Coal to Gasifier
Stream No.	5	6	7	8
Rate, lbs/hr	5800	4200	1018	1276
Analysis				
H_2	-	-	-	-
CO_2	-	-	-	-
CH_4	-	-	-	-
O_2	-	-	-	-
C_2H_6	-	-	-	-
N_2	-	-	-	-
H_2O	-	-	-	-
CO	-	-	-	-
Light Oil	-	-	-	-
Middle Oil	-	-	-	-
Heavy Oil	-	-	-	-
Moisture	232	168	41	51
MF Coal	5568	4032	977	1225
Total	5800	4200	1018	1276
Press., psig	Atmos.	Atmos.	200	150(max)
Temp., °F	200	200	175	175

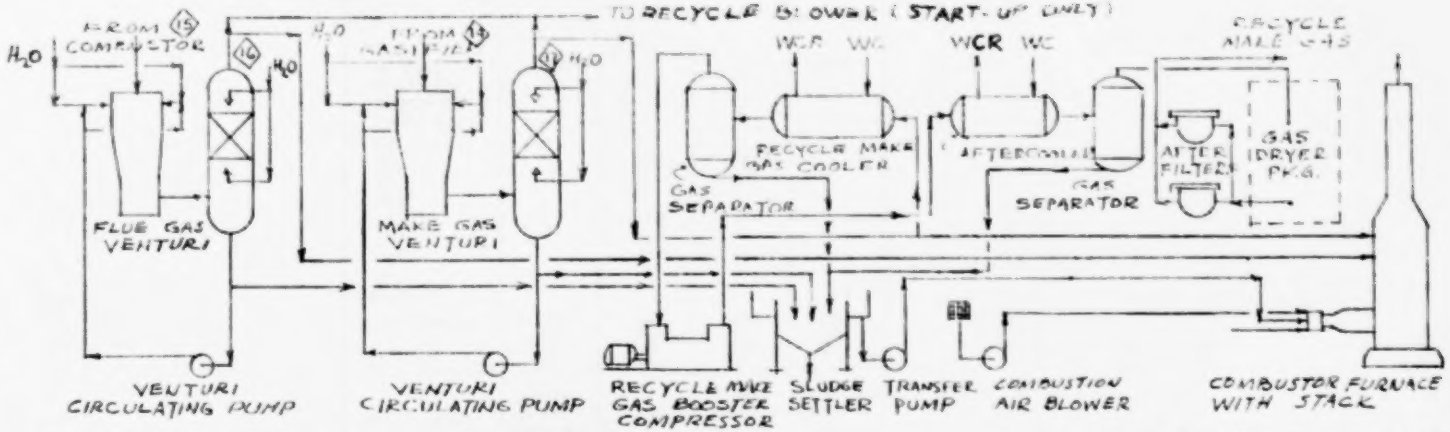

11
COMBUSTOR
ASH
22
COAL FEED (INERT GAS)
9
10
COAL & AIR
STEAM
AIR
23
24
COMBUSTOR ASH LETDOWN HOPPER
COMPR AIR
TOTE BIN
GASIFIER
STM
INERT GAS
GASIFIER ASH LETDOWN HOPPER
INERT BLANKET AIR
CHAR RECEIVING HOPPER
CHAR LETDOWN HOPPER
INERT BLANKET GAS
COOLER CONVEYOR RECEIVING HOPPER
CWR
CW
TOTE BIN
TO SCRUBBER
GASIFIER CYCLONE
GASIFIER CYCLONE RECEIVING HOPPER
GASIFIER CYCLONE LETDOWN HOPPER
INERT BLANKET GAS
TO SCRUBBER
COMBUSTOR CYCLONE
COMB. CYCLONE RECEIVING HOPPER
COMB. CYCLONE LETDOWN HOPPER
COMPR. AIR
TOTE BIN

GASIFICATION
AGGLOMERATING BURNER PLANT

SOURCE: BATTELE'S COLUMBUS LABS DRAWINGS OF 1974.

MATERIAL BALANCE

Stream Ident.	Coal to Gasifier	Coal to Combustor	Combustor Off-Gas	Gasifier Off-Gas	Char	Gasifier Gas to Scrubber	Combustor Gas to Scrubber	Ash from Combustor to Gasifier	Ash from Gasifier to Combustor	Ash from Combustor to Letdown Hopper
Stream No.	9	10	11	12	13	14	15	22	23	24
Rate, lbs/hr	1279	1165	12042	2840	244	2295	11993	41041	44102	47
Analysis										
H_2	5	-	-	191	-	191	-	-	-	-
CO_2	13	-	2690	471	-	31	2690	-	-	-
CH_4	-	-	-	-	-	-	-	-	-	-
O_2	-	45	259	-	-	-	259	-	586	-
C_2H_6	-	-	-	-	-	-	-	-	-	-
N_2	-	143	8539	14	-	14	8539	-	1925	-
H_2O	-	-	452	584	-	584	452	450	-	-
CO	36	-	-	1448	-	1448	-	-	-	-
Light Oil	-	-	-	-	-	-	-	-	-	-
Middle Oil	-	-	-	-	-	-	-	-	-	-
SO_2	-	-	47	-	-	-	47	-	-	-
H_2S	-	-	-	27	-	27	-	-	-	-
Ash	-	-	55	-	-	-	6	40591	41591	47
MF Coal	1225	977	-	-	-	-	-	-	-	-
Char	-	-	-	105	244	-	-	-	-	-
Total	1279	1165	12042	2840	244	2295	11993	41041	44102	47
Press., psig	150(max)	120(max)	100	100	100	100	100	100	100	100
Temp., °F	175(max)	175(max)	2050	1800	1800	180	2050	2050	1500	2050

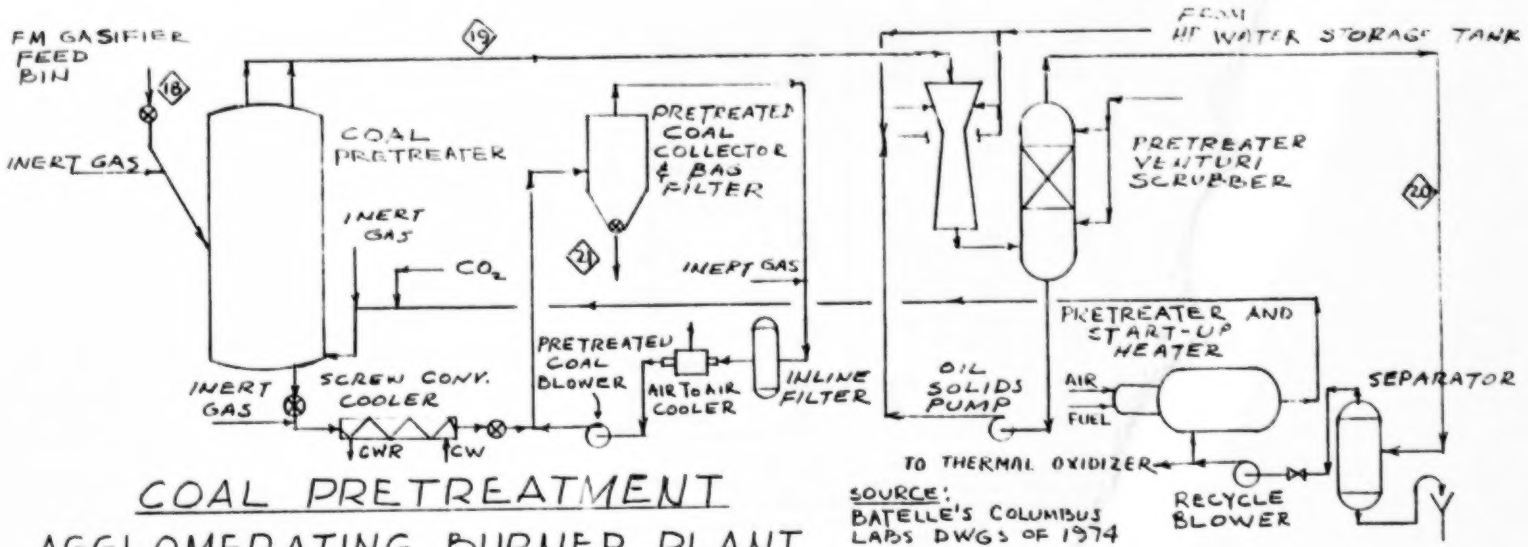

H_2O
FROM ⑮ COMBUSTOR
⑯
H_2O
FLUE GAS VENTURI
H_2O
FROM ⑭ GASIFIER
⑰
H_2O
MAKE GAS VENTURI
TO RECYCLE BLOWER (START-UP ONLY)
WCR WC
WCR WC
RECYCLE MAKE GAS
GAS SEPARATOR
RECYCLE MAKE GAS COOLER
AFTERCOOLER
GAS SEPARATOR
AFTER FILTERS
GAS DRYER PKG.
VENTURI CIRCULATING PUMP
VENTURI CIRCULATING PUMP
RECYCLE MAKE GAS BOOSTER COMPRESSOR
SLUDGE SETTLER
TRANSFER PUMP
COMBUSTION AIR BLOWER
COMBUSTOR FURNACE WITH STACK

SOURCE: BATELLE'S COLUMBUS LABS DRAWINGS OF 1974.

GAS TREATMENT

AGGLOMERATING BURNER PLANT

MATERIAL BALANCE				
Stream Ident.	Gasifier Gas to Scrubber	Combustor Gas to Scrubber	Combustor Gas to Combustor Furnace	Gasifier Gas to Combustor Furnace
Stream No.	⑭	⑮	⑯	⑰
Rate, lbs/hr	2295	11993	17292	4774
Analysis				
H_2	191	-	-	191
CO_2	31	2690	2690	471
CH_4	-	-	-	-
O_2	-	259	259	-
C_2H_6	-	-	-	-
N_2	14	8539	8539	14
H_2O	584	452	5757	2623
CO	1446	-	-	1448
Light Oil	-	-	-	-
Middle Oil	-	-	-	-
Heavy Oil	-	-	-	-
SO_2	-	47	47	-
H_2S	27	-	-	27
Total	2295	11993	17292	4774
Press., psig	100	100	90	90
Temp., °F	100	2050	279	281


FM GASIFIER FEED BIN
18
INERT GAS
19
COAL PRETREATER
INERT GAS
CO₂
INERT GAS
SCREW CONV. COOLER
CWR
CW
PRETREATED COAL COLLECTOR & BAG FILTER
21
INERT GAS
PRETREATED COAL BLOWER
AIR TO AIR COOLER
INLINE FILTER
FROM HP WATER STORAGE TANK
PRETREATER VENTURI SCRUBBER
20
OIL SOLIDS PUMP
PRETREATER AND START-UP HEATER
AIR
FUEL
TO THERMAL OXIDIZER
RECYCLE BLOWER
SEPARATOR

COAL PRETREATMENT

AGGLOMERATING BURNER PLANT

SOURCE:
BATELLE'S COLUMBUS LABS DWGS OF 1974

MATERIAL BALANCE				
Stream Ident.	Gasifier Feed Bin To Pre-treater	Gas From Pretreater	Pretreater Gas To Combustor Furnace	Pretreater Coal To Gasifier Feed Bin
Stream No.	18	19	20	21
Rate, lbs/hr	1339	1315	1455	1225
Analysis				
H_2	-	-	-	-
CO_2	-	194	194	-
CH_4	-	-	-	-
O_2	-	19	19	-
C_2H_6	-	-	-	-
N_2	-	701	701	-
H_2O	-	360	541	-
CO	-	-	-	-
Light Oil	-	41	-	-
Middle Oil	-		-	-
Heavy Oil	-		-	-
MF Coal	1339	-	-	1225
Solids	-	Trace	-	-
Total	1339	1315	1455	1225
Press., psig	Atmos.	-10*	-30*	Atmos.
Temp., °F	175	750	175	250

* Inches of water.

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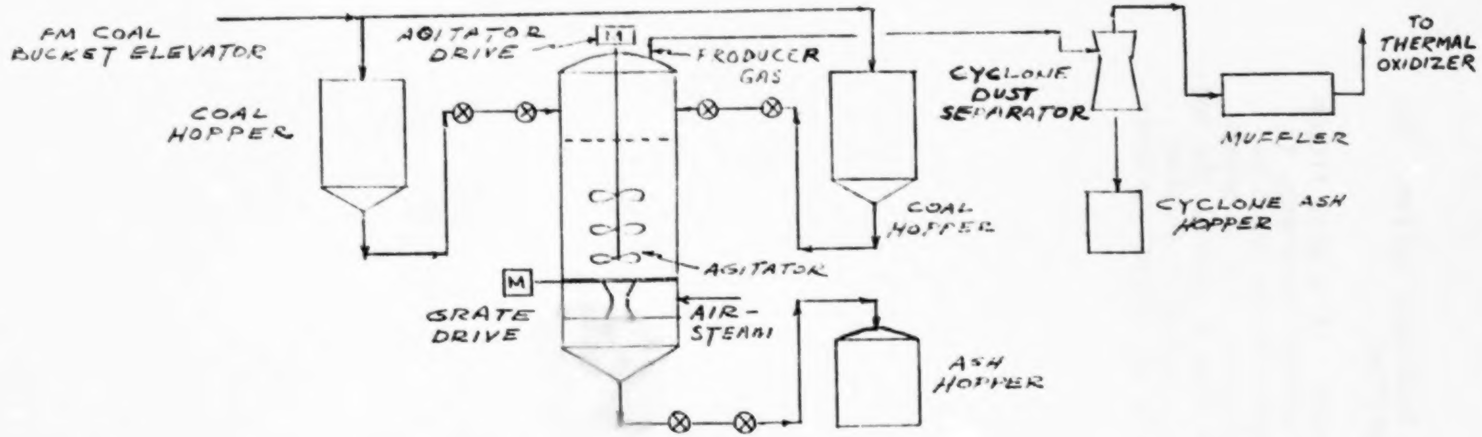
MERC STIRRED FIXED BED

Coal is broken to 2.0 x 0 inches and fed into a normal lockhopper system. The coal is then fed directly from the lockhopper to the gasifier.

The gasifier is a fixed-bed unit with a rotating ash grate. It is also fitted with a vertical agitator, capable of both rotation and vertical movement, to insure uniform distribution of coal in the bed and to break up agglomerates. The reactor operates at 2500°F (1370°C) and at up to 300 psig. Air or oxygen and steam enter the reactor below the grate so that gas flow is through the bed. The product gas is removed from the top of the reactor to a venturi scrubber, which cools the product for sampling before it is sent to the thermal oxidizer.


FM COAL BUCKET ELEVATOR
COAL HOPPER
AGITATOR DRIVE
M
PRODUCER GAS
AGITATOR
GRATE DRIVE
M
AIR - STEAM
COAL HOPPER
ASH HOPPER
CYCLONE DUST SEPARATOR
CYCLONE ASH HOPPER
MUFFLER
TO THERMAL OXIDIZER

GASIFICATION

MERC - STIRRED FIXED BED PILOT PLANT

SOURCE: MERC-ERDA DRAWINGS OF 1975.

Operating Data, Test Results:

Feed Coal	West Virginia Pittsburgh Bed	New Mexico Sub-bituminous
HHV of coal, Btu/lb	13,850	8,900
Gas Analysis		
CO	19.1	15.3
CO_2	8.8	12.7
N_2	55.4	59.3
H_2	12.8	10.7
CH_4	2.9	2.1
C_2H_6	.3	.0
H_2S	.5	.2
Heating Value Btu/scf	140	105

STEAM-IRON

For the pilot plant, char is crushed to 0.06-inch diameter (12 mesh), mixed as a water slurry, and pumped to 1000 psig. The slurry is vaporized and the steam conveys the char to the top of the preheater. The steam-iron process has two reactors — the producer and the steam-iron reactor.

The producer is a vertical, two-stage reactor. The char is fed into a char bed in the top section (preheater) and partially oxidized with steam and air at 1750°F (950°C). Off-gas is removed from the top and the hot char drops to the bottom stage to make a fluidized bed with steam and air. The char reacts at 2000°F (1090°C) to produce H_2 and CO, which is removed from the top of the lower stage. Ash is removed from the bottom of the reactor.

The H_2 and CO enter the top section of the vertical, two-stage iron-steam reactor, and fluidize a bed of iron oxide at 1500°F (815°C). In the bed the producer gas and iron oxide react to reduce the oxide to iron as follows:

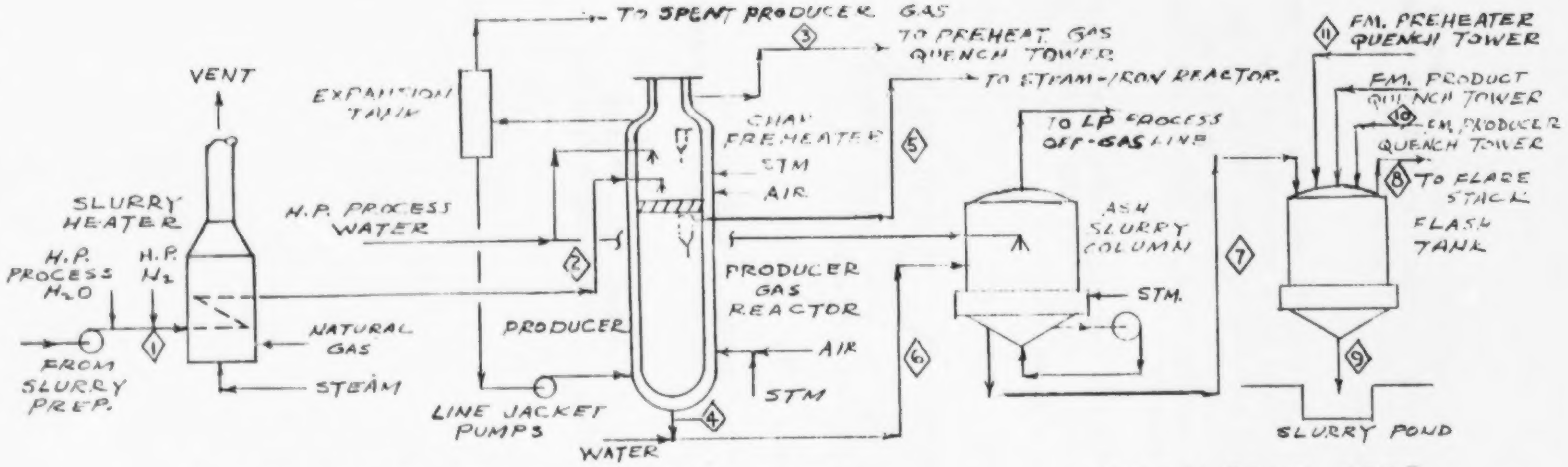
$$Fe_3O_4 + 2H_2 + CO \longrightarrow 3Fe + 2H_2O + CO_2$$

The upper stage has two sections for greater efficiency. The spent gas is removed from the top of the reactor, and the iron falls to the lower stage, creating a bed fluidized by steam. It is here that the iron reacts with the dissociated steam to form hydrogen and iron oxide, as follows:

$$4H_2O + 3Fe \longrightarrow Fe_3O_4 + 4H_2$$

The iron oxide is recycled to the top stage of the reactor and the H_2 is removed from the top of the lower stage, which also has two sections for greater efficiency.

At the present time, char residues are discharged, slurried, cooled, and separated out in a settling pond. The H_2 and off-gases are being thermally oxidized.


TO SPENT PRODUCER GAS
TO PREHEAT GAS QUENCH TOWER
TO STEAM-IRON REACTOR
FM. PREHEATER QUENCH TOWER
FM. PRODUCT QUENCH TOWER
FM. PRODUCER QUENCH TOWER
TO FLARE STACK
FLASH TANK
VENT
EXPANSION TANK
CHAR PREHEATER
STM
AIR
TO LP PROCESS OFF-GAS LINE
ASH SLURRY COLUMN
SLURRY HEATER
H.P. PROCESS WATER
H.P. PROCESS H₂O
H.P. N₂
FROM SLURRY PREP.
NATURAL GAS
STEAM
PRODUCER
PRODUCER GAS REACTOR
LINE JACKET PUMPS
WATER
STM.
SLURRY POND
1
2
3
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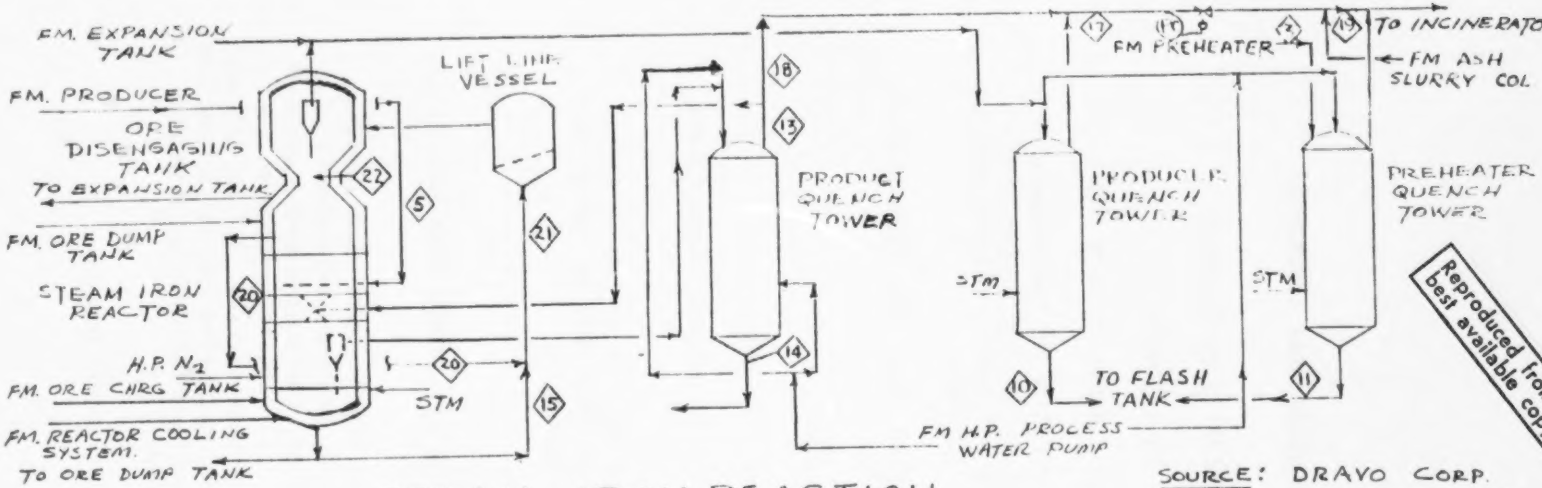
11

REDUCING GAS PRODUCTION
STEAM-IRON PILOT PLANT

SOURCE: DRAVO CORP. DRAWINGS OF 1974.

MATERIAL BALANCE											
Stream Ident.	Char Slurry	Preheater Feed	Preheat Off-Gas	Ash	Producer Gas	Ash Flume	Slurry to Flash Tank	Flash Tank Off-Gas	Flash Tank Slurry	Producer Quench Bleed	Preheat Quench Bleed
Stream No.	1	2	3	4	5	6	7	8	9	10	11
Rate, lbs/hr	10758	10758	10114	1061	12815	2065	14666	199	38206	10252	8427
Analysis											
H_2	-	-	10	-	170	-	-	7	<0.02	3	<0.3
CO_2	-	-	695	-	1144	-	-	58	4	54	8
CH_4	-	-	-	-	86	-	-	1	-	-	-
O_2	-	-	-	-	-	-	-	-	-	-	-
C_2H_6	-	-	-	-	-	-	-	-	-	-	-
N_2	-	-	1717	-	6341	-	-	95	Trace	73	22
H_2O	6992	6992	7498	10	582	1014	13615	14	36956	10000	8355
CO	-	-	134	-	4342	-	-	23	1	21	2
Coke/Char	2918	2918	31	279	101	279	279	-	410	66	31
Ash	788	788	8	752	27	752	752	-	788	18	8
H_2S	-	-	20	-	20	-	-	1	<0.4	<0.1	<0.3
S	60	60	1	20	2	20	20	-	23	1	1
Iron Solids	-	-	-	-	-	-	-	-	24	15	-
Total	10758	10758	10114	1061	12815	2065	14666	199	38206	10252	8427
Press., psig	1200	1070	1020	1070	1030	1070	1070	25	25	1000	1000
Temp., °F	73	600	852	1400	2000	807	200	144	144	114	110


FM. EXPANSION TANK
FM. PRODUCER
ORE DISENGAGING TANK
TO EXPANSION TANK
FM. ORE DUMP TANK
STEAM IRON REACTOR
H.P. N_2
FM. ORE CHRG TANK
FM. REACTOR COOLING SYSTEM.
TO ORE DUMP TANK
LIFT LINE VESSEL
PRODUCT QUENCH TOWER
PRODUCER QUENCH TOWER
PREHEATER QUENCH TOWER
STM
STM
STM
STM
TO FLASH TANK
FM H.P. PROCESS WATER PUMP
FM PREHEATER
TO INCINERATOR
FM ASH SLURRY COL
22
5
21
20
20
15
18
13
14
10
11
17
19
3

SOURCE: DRAVO CORP. DRAWINGS OF 1974.

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STEAM-IRON REACTION

STEAM-IRON PILOT PLANT

MATERIAL BALANCE

Stream Ident.	Preheat Off-Gas	Producer Gas	Producer Quench Tower Bleed	Preheat Quench Tower Bleed	Hydrogen from S-1 Reactor	Product Quench Off-Gas	Product Quench Bleed	Lift Line Dense Phase	Cooled Preheat Off-Gas	Quenched Product and Producer Gas	Product Gases	Low Pressure Off-Gas	Upper Reducer Spent Gas	Lift Line Dilute Phase	Iron Solids Recycle
Stream No.	3	5	10	11	12	13	14	15	16	17	18	19	20	21	22
Rate, lbs/hr	10114	12815	10252	8427	3962	5982	5060	186012	10911	28912	5063	28910	16421	202433	185424
Analysis															
H_2	10	170	3	<0.3	284	280	4	-	10	343	236	343	117	117	8
CO_2	695	1144	54	8	-	-	-	-	687	5029	-	5029	5464	5464	381
CH_4	-	86	1	-	-	-	-	-	-	85	-	85	92	92	6
O_2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
C_2H_6	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
N_2	1717	6341	73	22	63	63	<0.1	-	1696	6422	53	6422	6924	6924	482
H_2O	7498	582	10000	8355	3543	5623	5000	-	8365	15199	4760	15197	1761	3600	251
CO	134	4342	21	2	-	-	-	-	133	1814	-	1814	1972	1972	137
Light Oil	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Middle Oil	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Coke/Char	31	101	66	31	36	-	36	-	-	-	-	-	66	66	-
Ash	8	27	18	8	10	-	10	-	-	-	-	-	18	18	-
H_2S	20	20	<0.1	<0.3	17	16	<0.1	1838	20	20	14	20	6	6	<0.8
S	1	2	1	1	-	-	1	-	-	-	-	-	1	1	-
Iron Solids	-	-	15	-	9	-	9	184174	-	-	-	-	-	184173	184159
Total	10114	12815	10252	8427	3962	5982	5060	186012	10911	28912	5063	28910	16421	202433	185424
Press., psig	1020	1030	1000	1000	1050	1040	1040	1075	1000	1000	1040	25	1000	1000	1000
Temp., °F	852	2000	114	110	1460	597	105	1440	593	595	597	540	1400	1400	1400

GLOSSARY

ACGIH	American Conference of Governmental Industrial Hygienists.
ABRADE	To rub or wear away, especially by friction.
ABSORPTION	The dissolution of a gas in a liquid.
ACID GAS	Hydrogen sulfide (H_2S) and carbon dioxide (CO_2).
ACTIVATED CARBON	Carbon obtained by carbonization in the absence of air, preferably in a vacuum; has the property of absorbing large quantities of gases, solvent vapors; used also for clarifying liquids.
ACUTE	Having a sudden onset, sharp rise, and short course; demanding urgent attention.
ADA	Anthraquinone disulfide acid.
ADENOMA	A neoplasm of glandular epithelium.
ADSORPTION	The physical and chemical adherence of a gas to the surface of a solid.
AEROSOL	A suspension (in a body of gas) of liquid or solid particles of such size that they tend to remain suspended for an indefinite period.
AGA	American Gas Association.
AGGLOMERATE	Assemblage of particles rigidly joined together, as by partial fusion (sintering).
ALIPHATIC	One of the major groups of organic compounds characterized by straight-chain or branched arrangement of the constituent carbon atmos. [Aliphatic hydrocarbons include three subgroups: (1) paraffins (alkanes), which are saturated and unreactive; (2) olefins (alkenes or alkadienes), which are unsaturated and quite reactive; and (3) acetylenes (alkynes), which contain a triple bond and are highly reactive.]
AMBIENT	An encompassing atmosphere: environment.

AMINE	Any of various basic compounds derived from ammonia by replacement of hydrogen by one or more univalent hydrocarbon radicals.
AROMATIC (ARENE)	A major group of unsaturated cyclic hydrocarbons containing one or more rings (e.g., benzene). (These highly reactive and chemically versatile compounds have a strong, but not unpleasant, odor--thus the name "aromatic.")
AROMATIC HYDROCARBON	An unsaturated cyclic hydrocarbon containing one or more six-carbon rings.
ASH	Theoretically, the inorganic salts contained in coal; practically, the residue from the combustion of dried coal that has been burned at 1,380°F for an extended period of time.
BAFFLE	A device to deflect, check, or regulate flow.
BaP	Benzo[α]pyrene.
BATCH	The quantity produced at one operation without adding more feed.
BENCH PLANT STAGE	A small-scale laboratory unit for testing process concepts and operating parameters as a first step in the evaluation of a process.
BIOASSAY	An assay method using a change in biological activity as a qualitative or quantitative means of analyzing a material's response to biological treatment; a method of determining toxic effects of industrial wastes and other wastewaters by using viable organisms as test organisms.
BITUMEN	A general name for various solid and semisolid hydrocarbons; a native substance of dark color that is comparatively hard and nonvolatile and is composed principally of hydrocarbon.
BITUMINOUS COAL	A broad class of coals containing 46 to 86 percent fixed carbon and 20 to 40 percent volatile matter.
BSFTPM	Benzene-soluble fraction of total particulate matter. Also referred to as "benzene solubles."
BOILING FLUIDIZED BED	A fluidized bed through which part of the fluidizing medium passes in the form of bubbles of a size approximately equal to the size of the solid particles, but very small relative to the dimensions of the containing vessel.

Btu	British thermal unit, the quantity of energy required to raise the temperature of one pound of water one degree Fahrenheit.
BTX	Benzene, toluene, xylene; aromatic hydrocarbons.
BY-PRODUCTS (RESIDUALS)	Secondary products (possibly of commercial value) that are obtained from the processing of raw material. (By-products may be the residues of the gas production process [such as coke, tar, and ammonia] or they may be the result of further processing of such residues [such as ammonium sulfate].)
CAGE MILL	A common name for a Stedman Disintegrator. Mill consists of a number of parallel bars equally spaced around the circumference. Sizing is accomplished by the opening between bars.
CAKING	The softening and agglomeration of coal as a result of the application of heat.
CANCER	A malignant and invasive growth or tumor, especially one originating in epithelium.
CARBON STEAM REACTION	Water gas reaction whereby the passage of steam over carbon results in the formation of carbon monoxide and hydrogen.
CARBON TRAP ACTIVATED	A trap filled with activated carbon to prevent the passage of toxic gas.
CARBOXYHEMOGLOBINEMIA	The presence of carboxyhemoglobin (a compound formed from hemaglobin on exposure to carbon monoxide) in the blood.
CARCINOGEN	A substance or agent that produces or incites cancerous growth.
CARCINOMA	An epithelial cell, new growth, or malignant tumor that is enclosed in connective tissue and tends to infiltrate and give rise to metastases.
CARCINOMA IN SITU	A carcinoma that is confined to the site of origin, does not invade neighboring tissue.
CATALYST	In a chemical reaction, an extra substance that is usually used to speed up the reaction to produce the desired result. (The catalyst usually does not appear in the reaction product in any appreciable amount and therefore is not used up, as are the main ingredients in the reaction; the catalyst may have to be periodically discarded because of contamination.)

CAVITATION	The pitting and wearing away of solid surfaces (as of metal) as a result of the collapse of these vacuums in the surrounding liquid.
CHAR	The solid residue remaining after the removal of moisture and volatile matter from coal.
CHRONIC	Marked by long duration or frequent recurrence.
"CLOSED" SYSTEM	Any collection of matter within prescribed boundaries, which does not cross the boundaries.
COAL	A natural solid material consisting of amorphous elemental carbon with various amounts of organic and inorganic compounds.
COAL GAS	The gas that comes from retorts, mufflers, or ovens during the distillation of coal. (Coal gas has a high illuminating value and is a relatively suitable engine fuel. Large quantities of coal gas are produced when coal is used to make coke, coal tar, benzoil, toluene, ammonia, and other products.)
COAL GASIFICATION	The conversion of coal to a gas suitable for use as a fuel (HYGAS, CO_2 Acceptor, Bi-Gas, methanation, Lurgi ATGAS processes).
COAL GASIFICATION (HIGH-Btu GAS)	The combustion of coal at high temperatures (+1000°F) in an atmosphere deficient in oxygen (reducing) to produce a combustible gas.
COAL LIQUEFACTION (COAL HYDROGENATION)	The conversion of coal into liquid hydrocarbons and related compounds by hydrogenation.
COAL OIL	Oil obtained by the destructive distillation of bituminous coal; also an archaic term for kerosene made from petroleum.
COAL SLURRY	Pulverized coal suspended in a liquid.
COAL TAR	A gummy, black substance produced as a by-product of distillation of bituminous coal.
COALIFICATION	Metamorphosis of vegetable debris into coal.
COKE	Strong porous residue consisting of carbon and mineral ash formed when bituminous coal is heated in a limited air supply or in the absence of air. Coke may also be formed by thermal decomposition of petroleum residues.
COKE OVEN GAS	The gas secured from coke ovens during the production of coke. (The properties of this gas are identical to those of coal gas, and the two products are inter-

	changeable. Coke is particularly useful in making iron and steel and as an industrial fuel.)
CONDENSATE	Liquid hydrocarbon obtained by the combustion of a vapor or gas produced from oil or gas wells and ordinarily separated at a field separator and run as crude oil.
CRACKING	The partial decomposition of high-molecular-weight organic compounds into lower-molecular-weight compounds, generally as a result of high temperatures.
CYCLONE	A separator that depends upon centrifugal force to separate particles or droplets from the stream (used to separate solids from gases and water from steam).
CYTOLOGY	Branch of biology concerned with the study of cells as vital units with reference to their structure, function, multiplication, pathology, and life history.
DEGRADATION	A type of decomposition characteristic of high-molecular-weight substances such as proteins, polymers, and branched-chain sulfonates, resulting from oxidation, heat, solvents, and bacterial action.
DEHYDROGENATION	The process by which hydrogen is removed chemically from compounds.
DISPERSION	A suspension of particles in a medium; the opposite of flocculation; a scattering process.
DISTILLATION	A process of vaporizing a liquid and condensing the vapor by cooling; used for separating liquids into various fractions according to their boiling points or boiling ranges.
DOLOMITE	A mineral having the chemical formula CaMg $(CO_3)_2$, i.e., a carbonate of calcium and magnesium.
DOWTHERM	Trademark for a series of eutectic mixtures of diphenyl oxide and diphenyl used as high-temperature heat-transfer fluids.
DRY GAS	A gas that does not contain the heavier fractions, which may not easily condense under normal atmospheric conditions (e.g., methane and ethane).
DUST	A general term used to describe solid particles that are in the micron-size range (e.g., fly ash, coarse dirt, and mechanically produced particles.
EDEMA	The presence of abnormally large amounts of fluid in the intercellular tissue spaces of the body.

EFFLUENT	A discharge of pollutants into the environment, partially or completely treated or in its natural state (generally used in regard to discharges into waters).
ELECTROLYTE	A substance that when dissolved in a suitable solvent or when fused becomes an ionic conductor.
ELUTRIATION	The preferential removal of the small constituents of a mixture of solid particles by a stream of high-velocity gas.
EMULSION	A stable mixture of two or more immiscible liquids held in suspension by small percentages of substances called emulsifiers. [These are of two types: (1) proteins or carbohydrate polymers and (2) long-chain alcohols and fatty acids.]
ENDOTHERMIC	A chemical reaction that absorbs heat.
ENTRAIN	To draw in and transport (as solid particles or gas) by the flow of a fluid.
ENTRAINED BED (FLOW)	A bed in which solid particles are suspended in a moving fluid and are continuously carried over in the effluent stream.
EPIDEMIOLOGY	The study of diseases as they affect populations.
EXOTHERMIC	A reaction in which heat is liberated.
FILTER CAKE	The moist residue remaining from the filtration of a slurry to produce a clean filtrate.
FINES	In general, the smallest particle of coal or mineral in any classification, process, or sample of material; especially those that are elutriated from the main body of material in the process.
FIRST GENERATION	The first attempt at the development of an object or process.
FIXED BED	A bed in which the individual particles or granules of a solid are motionless and supported by contact with each other (in contrast with moving bed).
FLOTATION	A process for separating minerals from waste rock or solids of different kinds by agitating the pulverized mixture of solids with water, oil, and special chemicals, which causes preferential wetting of solid particles of certain types by the oil. (The unwetted particles are carried to the surface by the air bubbles and thus are separated from the wetted particles.) A frothing agent is also used to stabilize the bubbles

	in the form of a froth, which can easily be separated from the body of the liquid (froth flotation).
FLUE GAS, STACK GAS	Synonymous terms for the gases resulting from combustion of a fuel.
FLUIDIZATION (DENSE PHASE)	The turbulent motion of solid particles in a fluid stream; the particles are close enough to interact and give the appearance of a boiling liquid.
FLUIDIZATION (ENTRAINED)	Solid particles transported by a high-velocity fluid stream with little or no solid interaction.
FLUIDIZED BED	A bed of suitably sized solid particles through which a fluid (usually a gas) flows at a velocity high enough to buoy the particles, to overcome the influence of gravity, and to impart to them an appearance of great turbulence.
FROTHING	Vapor escaping from rapidly boiling liquid carries liquid with it causing bubbles to form, which impedes the reaction taking place.
ft/sec (fps)	Feet per second.
FUEL	A substance used to produce heat energy, chemical energy by combustion, or nuclear energy by nuclear fission.
g	Gram.
μg	Microgram.
GAS CHROMATOGRAPHY	(GC; gas-liquid chromatography, GLC; vapor-phase chromatography, VPC). The process in which the components of a mixture are separated from one another by volatilizing the sample into a carrier gas stream that is passing through and over a bed of packing consisting of a 20- to 200-mesh solid support. The surface of the latter is usually coated with a relatively nonvolatile liquid (the stationary phase). This gives rise to the term gas-liquid chromatograph. If the liquid is not present, the process is gas-solid chromatography which is also widely useful for analysis. Different components move through the bed of packing at different rates, and so appear one after another at the effluent end where they are detected and measured by thermal conductivity changes, density differences, or ionization detectors.
GASES	Materials that can be condensed to liquids only by pressure or at temperatures below ambient (such as oxygen, methane, hydrogen).

GAS LIQUOR (SOUR WATER)	The aqueous streams condensed from the coal conversion and processing areas by scrubbing and cooling of the crude gas stream.
GASIFICATION	In the most commonly used sense, refers to the conversion of coal to the high-Btu synthetic natural gas under conditions of high temperatures and pressures; in a more general sense, conversion of coal into a usable gas.
GASWORKS	Plants built during the 19th and early 20th centuries to produce gas. Coal was generally burned in reducing atmosphere with steam to form a low-Btu gas. The hot gas was passed through a brick checkerwork at atmospheric pressure to heat the brick. When the brick was hot, the gas was switched to a second checkerwork and oil was sprayed into the first. The gas produced from the two thermally cracked oil was added to the coal gas to form a medium (500-Btu) town gas.
GRAB SAMPLE	Obtaining a sample of an atmosphere in a very short period of time, so that this sampling time is insignificant in comparison with the duration of the operation or the period being studied.
HEAT RESERVOIR (SINK)	Anything that absorbs heat, usually part of the environment (such as the air, a river, or outer space).
HETEROCYCLIC	A cyclic or ring structure in which one or more of the atoms in the ring is an element other than carbon.
HIGH-Btu GAS	Fuel gas having a higher heating value of about 1000 Btu/scf or more.
HYDROCARBON	An organic compound consisting exclusively of the elements carbon and hydrogen. The principal types are aliphatic (straight-chain) and cyclic (closed ring). Aliphatic hydrocarbons include paraffins (alkanes), olefins (alkenes and alkadienes), acetylenes, and acyclic terpenes. Cyclic hydrocarbons include alicyclics (cycloparaffins, cycloolefins, cycloacetylenes); aromatics (benzene group [ring], naphthalene group [2 rings], anthracene group [3 rings]); and cyclic terpenes (monocyclic [dipentene], dicyclic [pinene]).
HYDROCRACKING	An oil-refining process in which the large molecules of crude oil are broken into smaller molecules through reaction with hydrogen. (The process is used to convert heavy oil into lighter fractions such as gasoline.)

HYDROGASIFICATION	Gasification that involves the direct reaction of fuels with hydrogen to optimize formation of methane.
HYDROGENATION	Chemical reactions involving the addition of gaseous hydrogen to a substance under high temperatures and pressures.
IN SITU	In its original place, e.g., underground gasification of a coal seam.
INERT GAS	A gas that does not react with other substances under ordinary conditions.
INORGANIC	Being or composed of matter other than plant or animal.
LEACHING	The process of extracting a soluble component from a mixture by percolation of the mixture with a solvent, usually water, resulting in the solution and later separation of the soluble component.
LIGHT GASOLINE, LIGHT NAPHTHA	Liquid C_5, C_6, C_7, C_8 derived from crude oil (about the same as condensate from raw natural gas).
LIGNITE	Brownish-black coal containing 65 to 72 percent carbon on a mineral-matter-free basis, with a rank between peat and sub-bituminous coal.
LIQUEFACTION	Conversion of a solid to a liquid; with coal, this appears to involve the thermal fracture of carbon-carbon and carbon-oxygen bonds, forming free radicals. The radicals abstract hydrogen atoms yielding low-molecular-weight gases and condensed aromatic liquids.
LOW-Btu GAS	A gas having a heating value of up to 350 Btu per standard cubic foot.
LOCKHOPPER	A mechanical device that permits the introduction of a solid into an environment of different pressure.
MAKE GAS/OIL/TAR	(Defined in text) Product gas--gas resulting from the gasification process.
METHANATION	The catalytic combination of carbon monoxide and hydrogen to produce methane and by-product water. (About 60% of the end-product methane is produced in the methanation step.)
MICRON	A unit of length equal to one millionth of a meter.
MORBIDITY	The relative incidence of disease.
MORTALITY	The number of deaths in a given time and place; the proportion of deaths to population.

MOVING BED	A body of solids in which the particles or granules of a solid remain in mutual contact, but in which the entire bed moves in piston-like fashion with respect to the containing walls (in contrast with fixed bed).
NARCOSIS	A reversible condition characterized by stupor or insensibility.
NEOPLASM	A new and abnormal formation of tissue, as a tumor or growth that serves no useful function but grows at the expense of the healthy organism.
OIL, GAS	An oil intermediate between the light distillates and the lubricating oils. (Most of the gas oil produced is turned over to the cracking apparatus for the production of gasoline and is used by gas companies for the manufacture of gas.)
ON-STREAM OPERATING TIME	The time during which the entire pilot plant is actually working at preset conditions, as opposed to the time in which it is shut down for repairs, is starting up, etc.
ORGANIC	Of, relating to, or containing carbon compounds.
OXIDATION	Originally meant a reaction in which oxygen combines chemically with another substance, but term now includes any reaction in which electrons are transferred.
PARTICULATE FLUIDIZED BED	A bed in such a condition of fluidization that the individual particles are discretely separated from each other and the volumetric concentration of solid particles is uniform throughout the bed.
PARTICULATES	Small particles of solid material produced by the burning of fuels.
PEAT	One of the earliest stages of coal in which the remains of plants and ferns that have been preserved may be clearly seen. (Peat contains a very high percentage of water and has been used as a fuel for hundreds of years in Ireland, England, and Germany.)
pH	A measure of the acidity or alkalinity of a material, liquid or solid. (pH is represented on a scale of 0 to 14, with 7 representing a neutral state, 0 representing the most acid, and 14 the most alkaline.)
PHOTOSENSITIZE	To make sensitive to the influence of radiant energy and especially light.
PILOT PLANT	A small-scale industrial process unit operated to test the application of a chemical or other manufacturing

	process under conditions that will yield information useful in design and operation of full-scale manufacturing equipment.
PIPELINE GAS	A methane-rich gas that conforms to certain standards and has a higher heating value between 950 and 1,050 Btu per standard cubic foot.
PITCH OF TAR	A black or dark brown solid or semisolid residue obtained by partial evaporation or fractional distillation of tars and tar products.
PNEUMOCONIOSIS	A chronic fibrous reaction in the lungs to the inhalation of dust.
POISONING OF A CATALYST	The deactivation of a catalyst by the addition of another substance, leaching of active metals, or destruction of crystal structure.
POLYMERIZATION	The reverse of cracking; a method of combining smaller molecules to make larger ones. (Polymerization was developed during the late 1930's to utilize refinery gases, which were often wasted or burned as fuel. The product of polymerization is usually "poly" gasoline; these fractions are high in antiknock value and are used primarily to raise the antiknock value of the finished gasoline.)
POLYNUCLEAR	Chemically polycyclic especially with respect to the benzene ring, used chiefly of aromatic hydrocarbons that are important as pollutants and possibly as carcinogens.
ppm	Parts of a substance per million parts of gas (air).
PROCESS POND WATER	Wastewater stored in the pond that was used in some way during the gasification process.
PROCESS STREAM	Any material stream within the coal conversion processing area.
PRODUCT STREAM	Streams within the coal conversion plant that contain the material which the plant was built to produce (e.g., oil, SNG, SRC).
psi	Pounds per square inch.
psig	Pounds per square inch, gauge.
PULMONARY	Pertaining to the lungs.
PYROLYSIS	Thermal decomposition of organic compounds in the absence of oxygen.

QUENCHING	Cooling by immersion in oil, water bath, or water spray.
RANK	Those differences in the pure coal material due to geological processes designated as metamorphic, whereby the coal material changes from peat through lignite and bituminous coal to anthracite or even to graphite; the degree of coal metamorphism.
RAW GAS	Impure gas produced in a gasifier.
REACTIVE CHAR	Char that is capable of spontaneously catching on fire while in strategic piles.
REACTOR	Vessel in which coal-conversion reactions take place.
REAL TIME	The actual time in which an event takes place with the reporting on or recording of the event practically simultaneous with its occurrence.
REDUCING ATMOSPHERE	At atmosphere that lowers the state of oxidation of chemicals within it.
REFRACTORY	A material capable of withstanding extremely high temperatures and having a relatively low thermal conductivity.
RESIDENCE TIME	The period of time during which a substance resides in a designated area.
RUN	The period during which a machine or plant is in continuous operation; the use of machinery for a single set of processing procedures.
SARCOMA	Cancer arising from underlying tissue, muscle, bone, and other connective tissue that may affect the bones, bladder, kidneys, liver, lung, parotids, and spleen.
scf	Standard cubic foot.
SCRUBBER	Apparatus in which a gas stream is freed of tar, ammonia, and hydrogen sulfide.
SECOND OPERATION	A type or class of objects or processes developed and improved from earlier objects or processes.
SENSIBLE HEAT	That heat that results in only the elevation of the temperature of a substance with no phase changes.
SHIFT CONVERSION	Process for the production of gas with a desired carbon monoxide content from crude gases derived from coal gasification; carbon-monoxide-rich gas is saturated with steam and passed through a catalytic

reactor where the carbon monoxide reacts with steam to produce hydrogen and carbon dioxide, the latter being subsequently removed in a scrubber employing a suitable sorbent.

SINTERING	The agglomeration of solids at temperatures below their melting point, usually as a consequence of heat and pressure.
SLUDGE	A soft mud, slush, or mire; e.g., the solid product of a filtration process before drying.
SLURRY	A suspension of pulverized solid in a liquid.
SMOG	Term used broadly to mean polluted air. (There are various types of smog which are produced from certain classes of pollutants under specific meteorologic conditions. Photochemical smog results from photochemical reactions involving hydrocarbons and nitrogen oxides.)
SMOKE	Solid and/or liquid particles formed by the incomplete combustion of fuels and discharged suspended in the gaseous combustion products.
SOOT	Agglomeration of tar-impregnated carbon particles that form when carbonaceous material does not undergo complete combustion.
SOUR GAS	A gas containing hydrogen sulfide.
SOUR WATER	See gas liquor.
STEADY STATE	A state or condition of a system or process that does not change in time.
SUB-BITUMINOUS COAL	Coal of intermediate rank (between lignite and bituminous); weathering and nonagglomerating coal having calorific values in the range of 8,300 to 13,000 Btu, calculated on a moist, mineral-matter-free basis.
SWEET GAS	Gas with H_2S removed.
SYNERGISM	The harmonious action of two agents (e.g., drugs) or organs (e.g., muscles) producing an effect neither could produce alone, or an effect that is greater than the total effect of each agent operating by itself.
SYNGAS	Synthetic gas (SNG).
SYNTHETIC NATURAL GAS (SNG)	Substitute natural gas; a manufactured gaseous fuel generally produced from naphtha or coal that contains 95% to 98% methane and has an energy content of 980 to 1,035 Btu/scf (about the same as that of natural gas).

TAR (COAL)	A dark brown or black, viscous, combustible liquid formed by the destructive distillation of coal.
TAR FOG	Submicron aerosol of condensed tar particles.
THERMOCYNAMICS, LAWS OF	The first law of thermodynamics states that energy can neither be created nor destroyed. The second law of thermodynamics states that when a free exchange of heat takes place between two bodies, the heat is always transferred from the warmer to the cooler body.
THRESHOLD LIMIT VALUE	Refers to airborne concentrations of substances and represents conditions under which it is believed that nearly all workers may be repeatedly exposed for an 8-hour day, 5 days a week (expressed as parts per million [ppm] for gases and vapors, and as milligrams per cubic meter [mg/m^3] for fumes, mists, and dusts).
TLC	Thin-layer chromatography.
TOXICANT	A substance that kills or injures an organism through chemical or physical action or by altering the organism's environment; for example, cyanides, phenols, pesticides, or heavy metals, especially used for insect control.
TRACE ELEMENTS	Elements found in small quantities or traces, usually because of their insolubility.
VAPOR	The gaseous form of a substance that is normally in the solid or liquid state at ambient conditions and which can be changed to the solid or liquid state by increasing the pressure and/or decreasing the temperature.
VARIABLE FUEL	A fuel substance that can be used in more than one form (e.g., solid, liquid, gas).
VENTING	Release of gases or vapors under pressure to the atmosphere.
VENTURI SCRUBBER	A gas-cleaning device that involves the injection of water into a stream of dust-laden gas flowing at a high velocity through a contracted portion of a duct, thus transferring the dust particles to the water droplets, which are subsequently removed.
VOLATILITY	That property of a liquid that denotes its tendency to vaporize.
WASHOUT	The removal of a pollutant by precipitation.

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